

EXHIBIT C

Publicly available information pertaining to the
Purification of TiCl₄ using Fatty Acids:

1. *Industrial Inorganic Pigments* (2nd Rev by Gunter Buxbaum), pages 60-87
2. U.S. Patent 3,009,772: Process for the purification of TiCl₄ (issued 1961)
3. U.S. Patent 3,963,585: Distillation of TiCl₄ in solution with selected amines (issued 1976)

2. White Pigments

White pigments include TiO_2 , zinc white (ZnO), zinc sulfide, lithopone (a mixed pigment produced from zinc sulfide and barium sulfate), and white lead (basic lead carbonate). The optical properties of white pigments are a result of their low light absorption and their strong, mainly nonselective, scattering of light.

2.1. Titanium Dioxide

Titanium dioxide [13463-67-7], TiO_2 , M_r 79.90, occurs in nature in the modifications rutile, anatase, and brookite. Rutile and anatase are produced industrially in large quantities and are used as pigments and catalysts, and in the production of ceramic and electronic materials.

Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties (which are superior to those of all other white pigments), its chemical stability, and lack of toxicity. Titanium dioxide is the most important inorganic pigment in terms of quantity, 3.2×10^6 t were produced in 1995. World production of titanium dioxide pigment is shown in Table 9 [2.1], [2.2], [2.3].

2.1.1. Properties [2.4], [2.5]

Physical Properties. Of the three modifications of TiO_2 , rutile is the most thermodynamically stable. Nevertheless, the lattice energies of the other phases are similar and hence are stable over long periods. Above 700°C , the monotropic conversion of anatase to rutile takes place rapidly. Brookite is difficult to produce, and therefore has no value in the TiO_2 pigment industry.

In all three TiO_2 modifications one titanium atom in the lattice is surrounded octahedrally by six oxygen atoms, and each oxygen atom is surrounded by three titanium atoms in a trigonal arrangement. The three modifications correspond to different ways of linking the octahedra at their corners and edges. Crystal lattice constants and densities are given in Table 10.

Rutile and anatase crystallize in the tetragonal system, brookite in the rhombic system. The melting point of TiO_2 is ca. 1800°C . Above 1000°C , the oxygen partial

Table 9. World production of TiO_2 pigment

Year	Sulfate process		Chloride process		Total 10^3 t/a
	10^3 t/a	%	10^3 t/a	%	
1965	1254	90.3	135	9.7	1389
1970	1499	77.4	437	22.6	1936
1977	1873	72.3	716	27.7	2589
1988	1781	60.2	1178	39.8	2959
1995	1481	46.0	1739	54.0	3220
2000*	1540	40	2310	60.0	3850

* Estimated.

Table 10. Crystallographic data for TiO_2 modifications

Phase	CAS registry no.	Crystal system	Lattice constants, nm			Density, g/cm ³
			<i>a</i>	<i>b</i>	<i>c</i>	
Rutile	[131-80-2]	tetragonal	0.4594		0.2958	4.21
Anatase	[1317-70-0]	tetragonal	0.3785		0.9514	4.06
Brookite	[12188-41-9]	rhombic	0.9184	0.5447	0.5145	4.13

pressure increases continuously as oxygen is liberated and lower oxides of titanium are formed. This is accompanied by changes in color and electrical conductivity. Above 400°C, a significant yellow color develops, caused by thermal expansion of the lattice; this is reversible. Rutile has the highest density and the most compact atomic structure, and is thus the hardest modification (Mohs hardness 6.5–7.0). Anatase is considerably softer (Mohs hardness 5.5).

Titanium dioxide is a light-sensitive semiconductor, and absorbs electromagnetic radiation in the near UV region. The energy difference between the valence and the conductivity bands in the solid state is 3.05 eV for rutile and 3.29 eV for anatase, corresponding to an absorption band at <415 nm for rutile and <385 nm for anatase.

Absorption of light energy causes an electron to be excited from the valence band to the conductivity band. This electron and the electron hole are mobile, and can move on the surface of the solid where they take part in redox reactions.

Chemical Properties. Titanium dioxide is amphoteric with very weak acidic and basic character. Accordingly, alkali-metal titanates and free titanic acids are unstable in water, forming amorphous titanium oxide hydroxides on hydrolysis.

Titanium dioxide is chemically very stable, and is not attacked by most organic and inorganic reagents. It dissolves in concentrated sulfuric acid and in hydrofluoric acid, and is attacked and dissolved by alkaline and acidic molten materials.

At high temperature, TiO_2 reacts with reducing agents such as carbon monoxide, hydrogen, and ammonia to form titanium oxides of lower valency; metallic titanium

is not formed. Titanium dioxide reacts with chlorine in the presence of carbon above 500 °C to form titanium tetrachloride.

Surface Properties of TiO₂ Pigments. The specific surface area of TiO₂ pigments can vary between 0.5 and 300 m²/g depending on its use. The surface of TiO₂ is saturated by coordinatively bonded water, which then forms hydroxyl ions. Depending on the type of bonding of the hydroxyl groups to the titanium, these groups possess acidic or basic character [2.6], [2.7]. The surface of TiO₂ is thus always polar. The surface covering of hydroxyl groups has a decisive influence on pigment properties such as dispersibility and weather resistance.

The presence of the hydroxyl groups makes photochemically-induced reactions possible, e.g., the decomposition of water into hydrogen and oxygen and the reduction of nitrogen to ammonia and hydrazine (see also Section 2.1.5) [2.8].

2.1.2. Raw Materials [2.9], [2.10]

The raw materials for TiO₂ production include natural products such as ilmenite, leucoxene, and rutile, and some very important synthetic materials such as titanium slag and synthetic rutile. Production values for the most important titanium-containing raw materials are listed in Table 11. Total production of titaniferous raw materials, excluding material produced and consumed in the former Soviet Union and China, grew in 1994 to 3.69 million tonnes of contained TiO₂ [2.11]. Australia was the largest producing country, followed by South Africa, Canada and Norway.

2.1.2.1. Natural Raw Materials

Titanium is the ninth most abundant element in the earth's crust, and always occurs in combination with oxygen. The more important titanium minerals are shown in Table 12. Of the natural titanium minerals, only ilmenite, leucoxene, and rutile are of economic importance. Leucoxene is a weathering product of ilmenite.

The largest titanium reserves in the world are in the form of anatase and titanomagnetite, but these cannot be worked economically at the present time. About 95% of the world's production of ilmenite and rutile is used to produce TiO₂ pigments, the remainder for the manufacture of titanium metal and in welding electrodes.

Ilmenite and Leucoxene. *Ilmenite* is found worldwide in primary massive ore deposits or as secondary alluvial deposits (sands) that contain heavy minerals. In the massive ores, the ilmenite is frequently associated with intermediary intrusions (Tellnes in Norway and Lake Allard in Canada). The concentrates obtained from these massive ores often have high iron contents in the form of segregated hematite or magnetite in the ilmenite. These reduce the TiO₂ content of the concentrates (see Table 13). Direct use of these ilmenites has decreased owing to their high iron

Table 11. Production of titanium-containing raw materials (1994)

Product	Country	Production (t/a)
Ilmenite*	Australia	1 770 000
	Canada	1 850 000
	India	280 000
	Norway	700 000
	Nouth Africa	1 500 000
	USA	320 000
	Former Soviet Union	250 000
	Other	450 000
	Total ilmenite	7 120 000
Rutile	Australia	216 000
	Sierra Leone	144 000
	South Africa	90 000
	Former Soviet Union	30 000
	Other	70 000
	Total rutile	550 000
Synthetic rutile	Australia	417 000
	India	43 000
	Japan	10 000
	Malaysia	15 000
	USA	140 000
	Total synthetic rutile	625 000
Titania slag	Canada	764 000
	Norway	170 000
	South Africa	773 000
	Total titania slag	1 707 000

* includes ilmenite used in the production of titania slag and synthetic rutile

Table 12. Titanium minerals

Mineral	Formula	TiO ₂ content (wt %)
Rutile	TiO ₂	92–98
Anatase	TiO ₂	90–95
Brookite	TiO ₂	90–100
Ilmenite	FeTiO ₃	35–60
Leucoxene	Fe ₂ O ₃ TiO ₂	60–90
Perovskite	CaTiO ₃	40–60
Sphene (titanite)	CaTiSiO ₅	30–42
Titanomagnetite	Fe(Ti)Fe ₂ O ₄	2–20

content. A digestion process is employed to produce iron sulfate heptahydrate. In cases where iron sulfate is not required as a product, metallurgical recovery of iron from the iron-rich ilmenites and production of a titanium-rich slag are being increasingly used.

Table 13. Composition of ilmenite deposits (wt %)

Component	Tellnes (Norway)	Richard's Bay (Republic of South Africa)	Capel (Western Australia)	Quilon (India)
TiO ₂	43.8	46.5	54.8	60.3
Fe ₂ O ₃	14.0	11.4	16.0	24.8
FeO	34.4	34.2	23.8	9.7
Al ₂ O ₃	0.6	1.3	1.0	1.0
SiO ₂	2.2	1.6	0.8	1.4
MnO	0.3	n.d.	1.5	0.4
Cr ₂ O ₃	n.d.	0.1	0.1	0.1
V ₂ O ₅	0.3	0.3	0.2	0.2
MgO	3.7	0.9	0.15	0.9

The enrichment of ilmenite in beach sand in existing or fossil coastlines is important for TiO₂ production. The action of surf, currents, and/or wind results in concentration of the ilmenite and other heavy minerals such as rutile, zircon, monazite, and other silicates in the dunes or beaches. This concentration process frequently leads to layering of the minerals. Attack by seawater and air over geological periods of time leads to corrosion of the ilmenite. Iron is removed from the ilmenite lattice, resulting in enrichment of the TiO₂ in the remaining material. The lattice is stable with TiO₂ contents up to ca. 65 %, but further removal of iron leads to the formation of a submicroscopic mixture of minerals which may include anatase, rutile, and amorphous phases. Mixtures with TiO₂ contents as high as 90 % are referred to as *leucoxene*. Leucoxene is present in corroded ilmenite and in some deposits is recovered and treated separately. However, the quantities produced are small in comparison to those of ilmenite.

The concentrates obtained from ilmenite sand, being depleted in iron, are generally richer in TiO₂ than those from the massive deposits. Other elements in these concentrates include magnesium, manganese, and vanadium (present in the ilmenite) and aluminum, calcium, chromium, and silicon which originate from mineral intrusions.

Two-thirds of the known ilmenite reserves that could be economically worked are in China, Norway (both massive deposits), and the former Soviet Union (sands and massive deposits). On the basis of current production capacities, these countries could cover all requirements for ca. 150 years. However, the countries with the largest outputs are Australia (sands), Canada (massive ore), and the Republic of South Africa (sands). Other producers are the United States (sands, Florida), India (sands, Quilon) the former Soviet Union (sands, massive ore), Sri Lanka (sands), and Brazil (rutile e ilmenita do Brasil). In 1994 the production of ilmenite was about 1.2×10^6 t of contained TiO₂.

Rutile is formed primarily by the crystallization of magma with high titanium and low iron contents, or by the metamorphosis of titanium-bearing sediments or magnetites. The rutile concentrations in primary rocks are not workable. Therefore, only sands in which rutile is accompanied by zircon and/or ilmenite and other heavy minerals can be regarded as reserves. The world reserves of rutile are estimated to

Table 14. Composition of rutile deposits [2.12]

Rutile component	Content (wt %)		
	Eastern Australia	Sierra Leone	Republic of South Africa
TiO ₂	96.00	95.70	95.40
Fe ₂ O ₃	0.70	0.90	0.70
Cr ₂ O ₃	0.27	0.23	0.10
MnO	0.02	n.d.	n.d.
Nb ₂ O ₅	0.45	0.21	0.32
V ₂ O ₅	0.50	1.00	0.65
ZrO ₂	0.50	0.67	0.46
Al ₂ O ₃	0.15	0.20	0.65
CaO	0.02	n.d.	0.05
P ₂ O ₅	0.02	0.04	0.02
SiO ₂	1.00	0.70	1.75

be 28×10^6 t, including the massive Piampaludo ore reserves in Italy, whose workability is in dispute.

As in the case of ilmenite, the largest producers are in Australia, the Republic of South Africa and Sierra Leone. There is not enough natural rutile to meet demand, and it is therefore gradually being replaced by the synthetic variety. In 1994 the world wide production of rutile was about 0.5×10^6 t of contained TiO₂. Compositions of typical rutile concentrates are given in Table 14.

Anatase, like rutile, is a modification of TiO₂. The largest reserves of this mineral are found in carboniferous intrusions in Brazil. Ore preparation techniques allow production of concentrates containing 80% TiO₂, with possible further concentration to 90% TiO₂ by treatment with hydrochloric acid [2.13]. The TiO₂ amount of these mineral deposits is estimated up to 100×10^6 t.

Ore Preparation. Most of the world's titanium ore production starts from heavy mineral sands. Figure 14 shows a schematic of the production process. The ilmenite is usually associated with rutile and zircon, so that ilmenite production is linked to the recovery of these minerals. Geological and hydrological conditions permitting, the raw sand (usually containing 3–10% heavy minerals) is obtained by wet dredging (a). After a sieve test (b), the raw sand is subjected to gravity concentration in several stages with Reichert cones (d) and/or spirals (e) to give a product containing 90–98% heavy minerals. This equipment separates the heavy from the light minerals (densities: 4.2–4.8 g/cm³ and < 3 g/cm³ respectively) [2.14].

The magnetic minerals (ilmenite) are then separated from the nonmagnetic (rutile, zircon, and silicates) by dry or wet magnetic separation (f). If the ores are from unweathered deposits, the magnetite must first be removed. An electrostatic separation stage (h) allows separation of harmful nonconducting mineral impurities such as granite, silicates, and phosphates from the ilmenite, which is a good conductor.

2.1. Titanium Dioxide 49

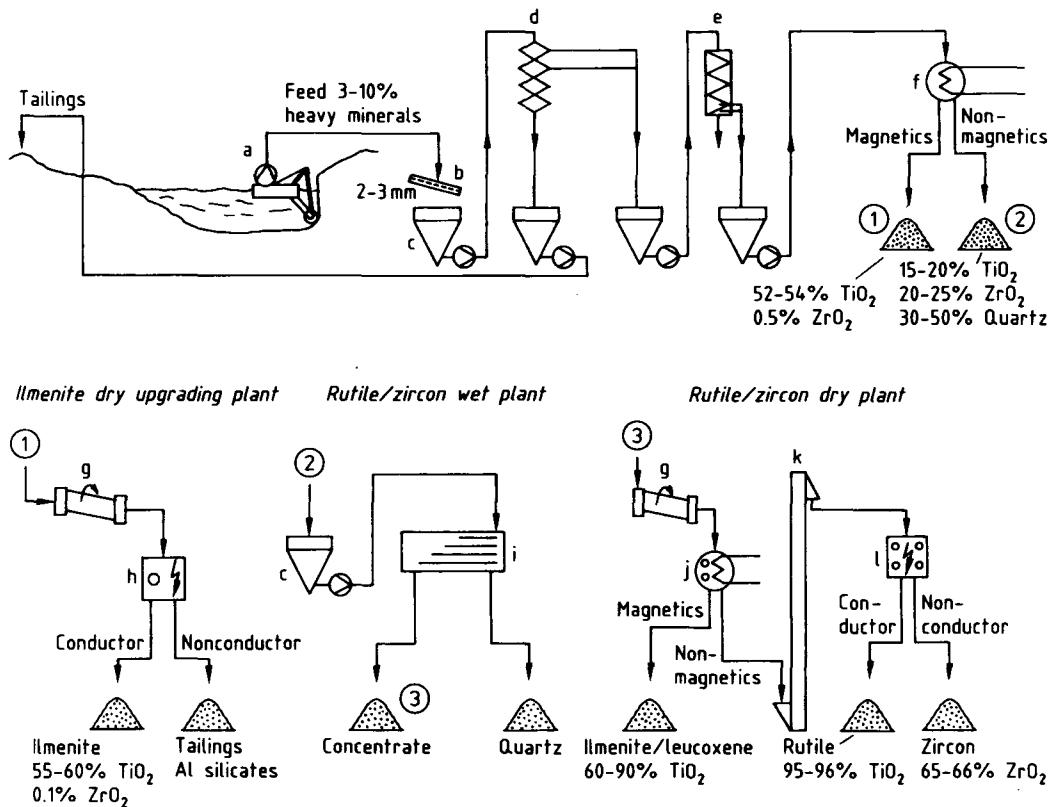


Figure 14. The processing of heavy mineral sands

a) Dredger; b) Sieve; c) Bunker; d) Reichert cones; e) Spirals; f) Magnetic separator; g) Dryer; h) Electrostatic separator; i) Shaking table; j) Dry magnetic separator; k) Vertical belt conveyor; l) Electrostatic separator

The nonmagnetic fraction (leucoxene, rutile, and zircon) then undergoes further hydromechanical processing (i) (shaking table, spirals) to remove the remaining low-density minerals (mostly quartz). Recovery of the weakly magnetic weathered ilmenites and leucoxenes is by high-intensity magnetic separation (j) in a final dry stage. The conducting rutile is then separated from the nonconducting zircon electrostatically in several stages (l). Residual quartz is removed by an air blast.

2.1.2.2. Synthetic Raw Materials

Increasing demand for raw materials with high TiO_2 content has led to the development of synthetic TiO_2 raw materials. In all production processes, iron is removed from ilmenites or titanomagnetites.

Titanium Slag. The metallurgical process for removing iron from ilmenite is based on slag formation in which the iron is reduced by anthracite or coke to metal at 1200–1600°C in an electric arc furnace, and then separated. Titanium-free pig iron is produced together with slags containing 70–85% TiO₂ (depending on the ore used) that can be digested with sulfuric acid because they are high in Ti³⁺ and low in carbon. Raw materials of this type are produced in Canada by the Quebec Iron and Titanium Corporation (QIT), in the Republic of South Africa by Richard's Bay Minerals (RBM), and to a smaller extent by Tinfos Titan and Iron K.S. (Tysseid, Norway). Total slag production grew in 1994 to 1.4×10^6 t of contained TiO₂.

Synthetic Rutile. In contrast to ilmenite, only a small number of rutile deposits can be mined economically, and the price of natural rutile is therefore high. Consequently, many different processes have been developed to remove the iron from ilmenite concentrates without changing the grain size of the mineral because this is highly suitable for the subsequent fluidized-bed chlorination process. All industrial processes involve reduction of Fe³⁺ with carbon or hydrogen, sometimes after preliminary activation of the ilmenite by oxidation. Depending on the reducing conditions, either Fe²⁺ is formed in an activated ilmenite lattice, or metallic iron is produced.

The activated Fe²⁺-containing ilmenite can be treated with hydrochloric or dilute sulfuric acid (preferably under pressure), and a “synthetic rutile” with a TiO₂ content of 85–96% is obtained [2.15]. The solutions containing iron(II) salts are concentrated and then thermally decomposed to form iron oxide and the free acid, which can be used again in the digestion process [2.16].

Metallic iron can be removed in various ways. The following processes are described in the patent literature:

- 1) Size reduction followed by physical processes such as magnetic separation or flotation
- 2) Dissolution in iron(III) chloride solutions [2.17], the resulting iron(II) salt is oxidized with air to give iron oxide hydroxides and iron(III) salts
- 3) Dissolution in acid
- 4) Oxidation with air in the presence of electrolytes. Various iron oxide or iron oxide hydroxide phases are formed depending on the electrolyte used: Possible electrolytes include iron(II) chloride solutions [2.18], ammonium chloride [2.19], or ammonium carbonate–carbonic acid [2.20]
- 5) Oxidation with the iron(III) sulfate from ilmenite digestion (see Section 2.1.3.1) [2.21], followed by crystallization of the iron(II) sulfate
- 6) Chlorination to form iron(III) chloride [2.22]
- 7) Reaction with carbon monoxide to form iron carbonyls [2.23] which can be decomposed to give high-purity iron

Another possible method of increasing the TiO₂ content of ilmenite is by partial chlorination of the iron in the presence of carbon. This is operated on a large scale by several companies [2.24], [2.25]. The most important companies which are producing synthetic rutile are located in Australia (Renison Goldfields Consolidated, Tiwest, Westralian Sands), United States (Kerr-McGee Synthetic Rutile), India (Kevala Minerals and Metals Ltd., DCW Ltd., Bene-Chlor Chemicals Ltd.), and Malaysia (Hitox). In 1994 production of synthetic rutile was about 0.6×10^6 t of contained TiO₂.

2.1.3. Production

Titanium dioxide pigments are produced by two different processes. The older *sulfate process* depends on the breakdown of the titanium-containing raw material ilmenite or titanium slag with concentrated sulfuric acid at 150–220 °C. Relatively pure TiO_2 dihydrate is precipitated by hydrolysis of the sulfate solution, which contains colored heavy metal sulfates, sometimes in high concentration. The impurities are largely removed in further purification stages. The hydrate is then calcined, ground, and further treated.

In the *chloride process*, the titanium-containing raw materials ilmenite, leucoxene, natural and synthetic rutile, titanium slag, and anatase are chlorinated at 700–1200 °C. Titanium tetrachloride is separated from other chlorides by distillation. Vanadium tetrachloride (VCl_4) and vanadium oxychloride (VOCl_3) must, however, first be reduced to solid chlorides. The TiCl_4 is burnt at temperatures of 900–1400 °C to form TiO_2 . This extremely pure pigment undergoes further treatment depending on the type of application.

2.1.3.1. Sulfate Method

The sulfate method is summarized in Figure 15.

Grinding. The titanium-bearing raw materials are dried to a moisture content of < 0.1 %. Drying is mainly intended to prevent heating and premature reaction on mixing with sulfuric acid. The raw materials are ground in ball mills to give a mean particle size of ca. 40 μm . The combination of grinding and drying shown in Figure 15 (a) is recommended. The small amount of metallic iron present in titanium slag is removed magnetically (c), which almost completely eliminates hydrogen evolution during subsequent digestion.

Digestion. *Batch digestion* is usually employed. The ground raw materials (ilmenite, titanium slag, or mixtures of the two) are mixed with 80–98 % H_2SO_4 . The ratio of H_2SO_4 to raw material is chosen so that the weight ratio of free H_2SO_4 to TiO_2 in the suspension produced by the hydrolysis is between 1.8 and 2.2 (the so-called “acid number”). The reaction in the digestion vessel (f) is started by adding water, dilute sulfuric acid, oleum, or sometimes steam. The temperature initially increases to 50–70 °C due to the heat of hydration of the acid. The exothermic sulfate formation then increases the temperature to 170–220 °C. If dilute acid or sparingly soluble raw materials are used, external heating is required.

After the maximum temperature has been reached, the reaction mixture must be left to mature for 1–12 h, depending on the raw material, so that the titanium-containing components become as soluble as possible. Digestion can be accelerated by blowing air through the mass while the temperature is increasing, and also during the maturing period.

Several *continuous digestion processes* have been proposed [2.26]. A proven method is to continuously feed a mixture of ilmenite and water together with the acid

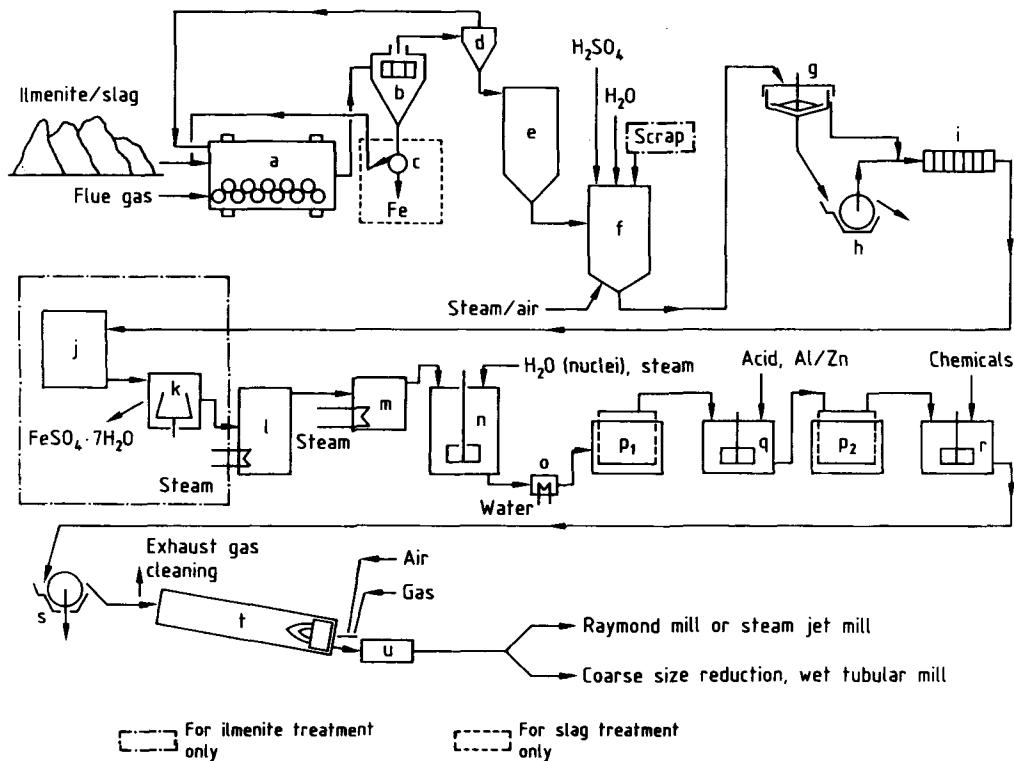


Figure 15. Production of TiO₂ by the sulfate process

a) Ball mill/dryer; b) Screen; c) Magnetic separator; d) Cyclone; e) Silo; f) Digestion vessel; g) Thickener; h) Rotary filter; i) Filter press; j) Crystallizer; k) Centrifuge; l) Vacuum evaporator; m) Preheater; n) Stirred tank for hydrolysis; o) Cooler; p₁) Moore filters; q) Stirred tank for bleaching; r) Stirred tank for doping; s) Rotary filter for dewatering; t) Rotary kiln; u) Cooler

into a double-paddle screw conveyor. After a relatively short dwell time (<1 h), a crumbly cake is produced [2.10]. This process utilizes a more limited range of raw materials than the batch process because they need to be very reactive.

Dissolution and Reduction. The cake obtained by digestion is dissolved in cold water or in dilute acid recycled from the process. A low temperature must be maintained (< 85°C) to avoid premature hydrolysis, especially with the product from ilmenite. Air is blown in to agitate the mixture during dissolution. With the ilmenite product, the TiO₂ concentration of the solution is 8–12 wt %, and with the slag product between 13 and 18 wt %.

The trivalent iron is hydrolyzed together with the titanium compounds, and adheres to the titanium oxide hydrate. Therefore all the Fe³⁺ is reduced to Fe²⁺ by scrap iron during dissolution of the ilmenite product, or immediately afterwards. Reoxidation of the iron during subsequent processing is prevented with Ti³⁺ which is obtained by reducing a small part of the Ti⁴⁺. Alternatively, reduction of Ti⁴⁺ to Ti³⁺ can be carried out in part of the solution under optimized conditions; this

concentrated Ti^{3+} solution is then added in a controlled manner to the reaction solution [2.27]. In solutions obtained from titanium slag, the Ti^{3+} content of the solution must be decreased by oxidation with atmospheric oxygen so that no loss of yield occurs during hydrolysis.

With both ilmenite and titanium slag, mixed digestion can be carried out in which the Ti^{3+} content of the slag reduces all the Fe^{3+} to Fe^{2+} . The dissolved products obtained from the separate digestion of ilmenite and titanium slag can also be mixed [2.28], [2.29].

Clarification. All undissolved solid material must be removed as completely as possible from the solution. The most economical method is to employ preliminary settling in a thickener (g), followed by filtration of the sediment with a rotary vacuum filter (h). The filtrate and the supernatant from the thickener are passed through filter presses (i) to remove fines. Owing to the poor filtering properties of the solution, the rotary filter must be operated as a precoat filter. Preliminary separation in the thickener must be assisted by adding chemicals to promote sedimentation. Attempts to carry out the entire clarification process in a single stage using automated filter presses have been reported [2.30].

Crystallization. The solutions from slag digestion contain 5–6 wt % FeSO_4 , and those from ilmenite digestion 16–20 wt % FeSO_4 after reduction of the Fe^{3+} . The solution is cooled under vacuum to crystallize out $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (j) and reduce the quantity of FeSO_4 discharged with the waste acid. The concentration of the TiO_2 in the solution is thereby increased by ca. 25 %. The salt is separated by filtration or centrifugation (k).

The iron sulfate is used in water purification, and as a raw material for the production of iron oxide pigments. Alternatively, it can be dehydrated and thermally decomposed to give iron(III) oxide and sulfur dioxide.

Hydrolysis. Titanium oxide hydrate is precipitated by hydrolysis at 94–110 °C. Other sulfuric-acid-soluble components of the raw material are precipitated simultaneously, mainly niobium as its oxide hydrate.

Hydrolysis is carried out in brick-lined, stirred tanks (n) into which steam is passed. The hydrolysate does not have any pigment properties, but these are strongly influenced by the particle size and degree of flocculation of the hydrolysate (mean particle size of hydrolysate is ca. 5 nm, and of TiO_2 pigments 200–300 nm).

The properties of the hydrolysate depend on several factors:

- 1) The hydrolysis of concentrated solutions of titanium sulfate (170–230 g TiO_2 /L) proceeds very sluggishly and incompletely (even if boiled) unless suitable nuclei are added or formed to accelerate hydrolysis. The nuclei are usually produced by two methods. In the Mecklenburg method, colloidal titanium oxide hydrate is precipitated with sodium hydroxide at 100 °C; 1% of this hydrate is sufficient. In the Blumenfeld method a small part of the sulfate solution is hydrolyzed in boiling water and then added to the bulk solution [2.31]. The particle size of the hydrolysate depends on the number of nuclei.
- 2) The particle size and degree of flocculation of the hydrolysate depend on the intensity of agitation during the nuclei formation by the Blumenfeld method and also during the initial stage of the hydrolysis.

- 3) The titanium sulfate concentration has a great influence on the flocculation of the hydrolysate. It is adjusted, if necessary by vacuum evaporation, to give a TiO_2 content of 170–230 g/L during hydrolysis. Lower concentrations result in a coarser particle size.
- 4) The acid number should be between 1.8 and 2.2. It has a considerable effect on the TiO_2 yield and on the particle size of the hydrolysate. For a normal hydrolysis period (3–6 h) the TiO_2 yield is 93–96 %.
- 5) The properties of the hydrolysate are affected by the concentrations of other salts present, especially FeSO_4 . High concentrations lead to finely divided hydrolysates.
- 6) The temperature regime mainly affects the volume–time yield and hence the purity of the hydrolysate.

Purification of the Hydrolysate. After hydrolysis, the liquid phase of the titanium oxide hydrate suspension contains 20–28 % H_2SO_4 and various amounts of dissolved sulfates, depending on the raw material. The hydrate is filtered off from the solution (p_1) (weak acid), and washed with water or dilute acid. Even with acid washing, too many heavy metal ions are adsorbed on the hydrate for it to be directly usable in the production of white pigment. Most of the impurities can be removed by reduction (bleaching), whereby the filter cake is slurried with dilute acid (3–10 %) at 50–90 °C and mixed with zinc or aluminum powder (q). Bleaching can also be carried out with powerful nonmetallic reducing agents (e.g., $\text{HOCH}_2\text{--SO}_2\text{Na}$). After a second filtration and washing process (p_2), the hydrate only has low concentrations (ppm) of colored impurities but still contains chemisorbed 5–10 % H_2SO_4 . This cannot be removed by washing and is driven off by heating to a high temperature.

Doping of the Hydrate. When producing titanium dioxide of maximum purity, the hydrate is heated (calcined) without any further additions. This gives a fairly coarse grade of TiO_2 with a rutile content that depends on the heating temperature. However, to produce specific pigment grades, the hydrate must be treated with alkali-metal compounds and phosphoric acid as mineralizers (< 1 %) prior to calcination (r). Anatase pigments contain more phosphoric acid than rutile pigments. To produce rutile pigments, rutile nuclei (< 10 %) must be added; ZnO , Al_2O_3 , and/or Sb_2O_3 (< 3 %) are sometimes also added to stabilize the crystal structure.

Nuclei are produced by converting the purified titanium oxide hydrate to sodium titanate, which is washed free of sulfate and then treated with hydrochloric acid to produce the rutile nuclei. Rutile nuclei can also be prepared by precipitation from titanium tetrachloride solutions with sodium hydroxide solution.

Calcination. The doped hydrate is filtered with rotary vacuum filters (s) to remove water until a TiO_2 content of ca. 30–40 % is reached. Pressure rotary filters or automatic filter presses can also be used to obtain a TiO_2 content of ca. 50 %. Some of the water-soluble dopants are lost in the filtrate and can be replaced by adding them to the filter cake before it is charged into the kiln. Calcination is performed in rotary kilns (t) directly heated with gas or oil in countercurrent flow. Approximately two-thirds of the residence time (7–20 h in total) is needed to dry the material. Above ca. 500 °C, sulfur trioxide is driven off which partially decomposes to sulfur dioxide and oxygen at higher temperatures. The product reaches a maximum temperature of 800–1100 °C depending on pigment type, throughput, and temperature

profile of the kiln. Rutile content, particle size, size distribution, and aggregate formation are extremely dependent on the operating regime of the kiln. After leaving the kiln, the clinker can be indirectly cooled or directly air-cooled in drum coolers (u).

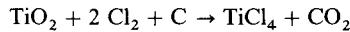
The exhaust gas must have a temperature of $> 300^{\circ}\text{C}$ at the exit of the kiln to prevent condensation of sulfuric acid in the ducting. Energy can be saved by recirculating some of the gas to the combustion chamber of the kiln and mixing it with the fuel gases as a partial replacement for air. Alternatively, it can be used for concentrating the dilute acid (see Section 2.1.3.5). The gas then goes to the waste-gas purification system.

Grinding. The agglomerates and aggregates in the clinker can be reduced to pigment fineness by wet or dry grinding. Coarse size reduction should be carried out in hammer mills prior to wet grinding in tube mills (with addition of wetting agents). The coarse fraction can be removed from the suspension by centrifugation, and recycled to the mills. Hammer mills, cross-beater mills, and particularly pendular and steam-jet mills are suitable for dry grinding. Special grinding additives can be used that act as wetting agents during subsequent pigment treatment or improve the dispersibility of untreated pigments.

2.1.3.2. The Chloride Process

The chloride process is summarized in Figure 16.

Chlorination. The titanium in the raw material is converted to titanium tetrachloride in a reducing atmosphere. Calcined petroleum coke is used as the reducing agent because it has an extremely low ash content and, due to its low volatiles content, very little HCl is formed. The titanium dioxide reacts exothermically as follows:



As the temperature rises, an endothermic reaction also occurs to an increasing extent in which carbon monoxide is formed from the carbon dioxide and carbon. Therefore, oxygen must be blown in with the chlorine to maintain the reaction temperature between 800 and 1200°C . The coke consumption per tonne of TiO_2 is 250–300 kg. If CO_2 -containing chlorine from the combustion of TiCl_4 is used, the coke consumption increases to 350–450 kg.

The older *fixed-bed chlorination method* is hardly used today. In this process, the ground titanium-containing raw material is mixed with petroleum coke and a binder, and formed into briquettes. Chlorination is carried out at 700–900 °C in brick-lined reactors.

Fluidized-bed chlorination was started in 1950. The titanium raw material (with a particle size similar to that of sand) and petroleum coke (with a mean particle size ca. five times that of the TiO_2) are reacted with chlorine and oxygen in a brick-lined fluidized-bed reactor (Fig. 16, c) at 800–1200 °C. The raw materials must be as dry as possible to avoid HCl formation. Since the only losses are those due to dust entrainment the chlorine is 98–100% reacted, and the titanium in the raw material

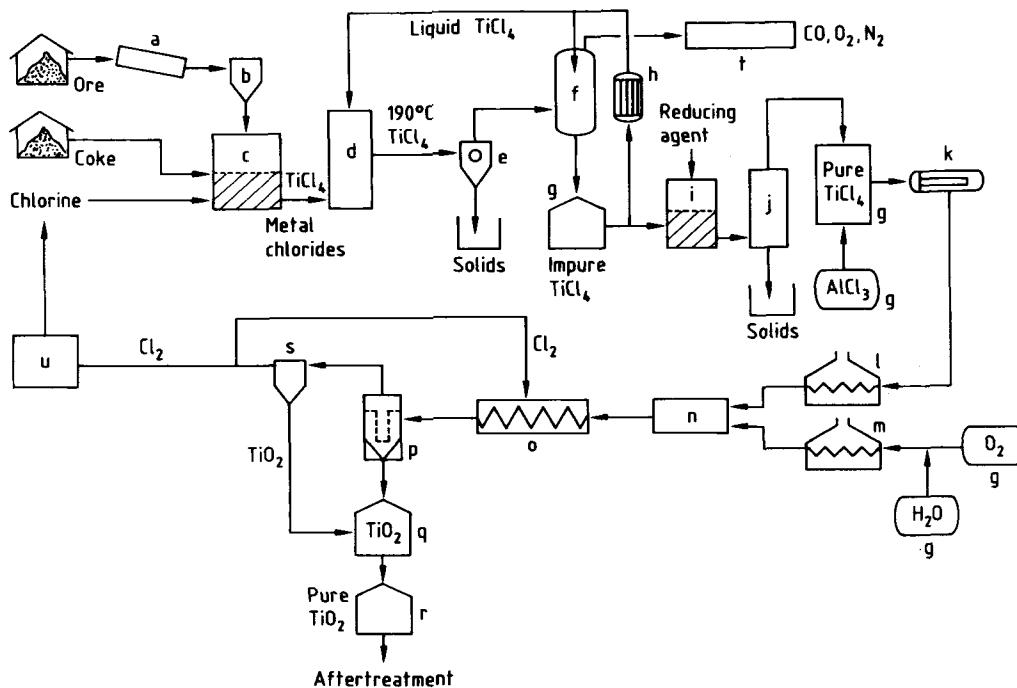


Figure 16. Flow diagram of TiO_2 production by the chloride process

a) Mill; b) Silo; c) Fluidized-bed reactor; d) Cooling tower; e) Separation of metal chlorides; f) TiCl_4 condensation; g) Tank; h) Cooler; i) Vanadium reduction; j) Distillation; k) Evaporator; l) TiCl_4 superheater; m) O_2 superheater; n) Burner; o) Cooling coil; p) Filter; q) TiO_2 purification; r) Silo; s) Gas purification; t) Waste-gas cleaning; u) Cl_2 liquefaction

is 95–100% reacted, depending on the reactor design and the gas velocity. Magnesium chloride and calcium chloride can accumulate in the fluidized-bed reactor due to their low volatility. Zirconium silicate also accumulates because it is chlorinated only very slowly at the temperatures used. All the other constituents of the raw materials are volatilized as chlorides in the reaction gases.

The ceramic cladding of the fluidized-bed reactor is rather rapidly destroyed by abrasion and corrosion. If chlorination is interrupted, there is a further danger that the raw materials may sinter and eventually cannot be fluidized.

Gas Cooling. The reaction gases are cooled with liquid TiCl_4 either indirectly or directly (d). Crystallization of the chlorides of the other components causes problems because they tend to build up on the cooling surfaces, especially the large quantities of iron(II) and iron(III) chlorides formed on chlorination of ilmenite [2.32]. In this first stage, the reaction gases are cooled only down to a temperature ($< 300^\circ\text{C}$) at which the accompanying chlorides can be satisfactorily separated from the TiCl_4 by condensation or sublimation (e).

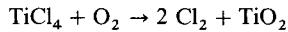
The gas then consists mainly of TiCl_4 , and is cooled below 0°C , causing most of the TiCl_4 to condense (f). The small amounts of TiCl_4 and Cl_2 remaining in the exhaust gas (CO_2 , CO , and N_2) are removed by scrubbing with alkali (t).

Purification of TiCl_4 . The chlorides that are solid at room temperature and the entrained dust can be separated from the TiCl_4 by simply evaporating (distilling) this off (j). Dissolved chlorine can be removed by heating or reduction with metal powders (Fe, Cu, or Sn).

Removal of vanadium tetrachloride (VCl_4) and vanadium oxychloride (VOCl_3) from the TiCl_4 by distillation is very difficult owing to the closeness of their boiling points. They are therefore reduced to form solid, low-value vanadium chlorides (i). **An enormous number of reducing agents have been recommended; important examples are copper, titanium trichloride, hydrogen sulfide, hydrocarbons, soaps, fatty acids, and amines.** After subsequent evaporation (j) the titanium chloride should contain < 5 ppm vanadium. If organic reducing agents are used, the residues may cause problems by baking onto the surfaces of the heat exchanger.

Phosgene and SiCl_4 can be removed by fractional distillation.

Combustion of TiCl_4 and Recovery of TiO_2 . Titanium tetrachloride is combusted with oxygen at 900–1400 °C to form TiO_2 pigment and chlorine (n). The purified TiCl_4 is vaporized (k) and the vapor is indirectly heated to ca. 500–1000 °C (l). The reaction



is weakly exothermic, and requires a high reaction temperature, so that the oxygen must also be heated to > 1000 °C (m). This can be achieved with an electric plasma flame, by reacting part of the oxygen with carbon monoxide, or by indirect heating. Hot TiCl_4 and oxygen (110–150 % of the stoichiometric amount) are fed separately into a reaction chamber where they must be mixed as rapidly and completely as possible to give a high reaction rate. For this reason, and also because the TiO_2 has a strong tendency to cake onto the walls [2.33]–[2.35], many different reactor designs have been proposed and used. The same considerations apply to the cooling unit (o) where the pigment is very rapidly cooled to below 600 °C. Cooling zones of various geometries are used. If caking occurs, the material can be removed by introducing abrasive particles [2.36], [2.37].

The mixture of gases (Cl_2 , O_2 , and CO_2) and pigment can be further cooled during dry separation of the pigment either indirectly or directly by solid particles, e.g., sand. The pigment-containing gas is then filtered (p). The gas stream is recycled to the cooling zone (o) of the combustion furnace and to the chlorination process as oxygen-containing chlorine via the liquefaction unit (u). The chlorine adsorbed on the pigment can be removed by heating or by flushing with nitrogen or air.

The wet separation process, in which the pigment-containing gas mixture (Cl_2 , O_2 , and CO_2) is quenched in water, has not become established.

2.1.3.3. Pigment Quality

The quality of the TiO_2 pigment is influenced by various factors. Reaction temperature, excess oxygen, and flow conditions in the reactor affect particle size and size distribution. Therefore, optimum conditions must be established for every reactor design. Caking of the TiO_2 on the walls of the reactor leads to impairment of quality.

The presence of water and a Cs-compound during combustion of the $TiCl_4$ gives rise to nuclei which promote the formation of finely divided pigment particles with high scattering power [2.38]. It can be added directly to the oxygen or can be produced by the combustion of hydrogen-containing materials.

The presence of $AlCl_3$ promotes the formation of rutile and a more finely divided pigment. It is added in amounts of up to 5 mol %. Many methods have been proposed for rapidly generating and directly introducing the $AlCl_3$ vapor into the $TiCl_4$ vapor. Addition of PCl_3 and $SiCl_4$ suppresses rutile formation, so that anatase pigment is obtained [2.39]. However, pigments of this type have not appeared on the market.

Pigments produced by the chloride process (chloride pigments) have better lightness and a more neutral hue than pigments produced by the sulfate process (sulfate pigments). Pigments used in demanding applications are almost always subjected to inorganic aftertreatment.

2.1.3.4. Aftertreatment

Aftertreatment of the pigment particles improves the weather resistance and lightfastness of the pigmented organic matrix, and dispersibility in this matrix. The treatment consists of coating the individual pigment particles with colorless inorganic compounds of low solubility by precipitating them onto the surface. However, this reduces the optical performance of the pigment approximately in proportion to the decrease in the TiO_2 content. The surface coatings prevent direct contact between the binder matrix and the reactive surface of the TiO_2 . The effectiveness of these coatings largely depends on their composition and method of application, which may give too porous or too dense a coating. The treatment process also affects the dispersibility of the pigment, and therefore a compromise often has to be made. High weather resistance and good dispersibility of the pigment in the binder or matrix are usually desired. These effects are controlled by using different coating densities and porosities. Other organic substances can be added during the final milling of the dried pigment.

Several types of treatment are used:

- 1) Deposition from the gas phase by hydrolysis or decomposition of volatile substances such as chlorides or organometallic compounds. Precipitation onto the pigment surface is brought about by adding water vapor. This method is especially applicable to chloride pigments, which are formed under dry conditions.
- 2) Addition of oxides, hydroxides, or substances that can be adsorbed onto the surface during pigment grinding. This can produce partial coating of the pigment surface.
- 3) Precipitation of the coating from aqueous solutions onto the suspended TiO_2 particles. Batch processes in stirred tanks are preferred; various compounds are deposited one after the other under optimum conditions. There is a very extensive patent literature on this subject. Continuous precipitation is sometimes used in mixing lines or cascades of stirred tanks. Coatings of widely differing compounds are produced in a variety of sequences. The most common are oxides, oxide hydrates, silicates, and/or phosphates of titanium, zirconium, silicon, and aluminum. For special applications, boron, tin, zinc, cerium, manganese, antimony, or vanadium compounds can be used [2.40], [2.41].

Three groups of pigments have very good lightfastness or weather resistance:

- 1) Pigments with dense surface coatings for paints or plastics formed by:
 - a) Homogeneous precipitation of SiO_2 with precise control of temperature, pH, and precipitation rate [2.42]: ca. 88% TiO_2
 - b) Two complete aftertreatments, calcination is performed at 500–800°C after the first or second aftertreatment [2.43]: ca. 91% TiO_2
 - c) Aftertreatment with Zr, Ti, Al, and Si compounds, sometimes followed by calcination at 700–800°C [2.44]: ca. 95% TiO_2
- 2) Pigments with porous coatings for use in emulsion paints obtained by simple treatment with Ti, Al, and Si compounds, giving a silica content of 10% and a TiO_2 content of 80–85%
- 3) Lightfast pigments with dense surface coatings for the paper industry that have a stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium, and aluminum: ca. 90% TiO_2

Coprecipitation of special cations such as antimony or cerium can improve lightfastness further [2.45]. After treatment in aqueous media, the pigments are washed on a rotary vacuum filter or a filter press until they are free of salt, and then dried using, e.g., belt, spray, or fluidized-bed dryers.

Before micronizing the pigment in air-jet or steam-jet mills, and sometimes also before drying, the pigment surface is improved by adding substances to improve dispersibility and facilitate further processing. The choice of compounds used, which are mostly organic, depends on the intended use of the pigment. The final surface can be made either hydrophobic (e.g., using silicones, organophosphates, and alkyl phthalates) or hydrophilic (e.g., using alcohols, esters, ethers and their polymers, amines, organic acids). Combinations of hydrophobic and hydrophilic substances have proved especially useful for obtaining surface properties that give better dispersibility and longer shelf life [2.46].

2.1.3.5. Problems with Aqueous and Gaseous Waste

Aqueous Waste. In the *sulfate process*, 2.4–3.5 t concentrated H_2SO_4 are used per tonne of TiO_2 produced, depending on the raw material. During processing, some of this sulfuric acid is converted to sulfate, primarily iron(II) sulfate, the rest is obtained as free sulfuric acid (weak acid). Filtration of the hydrolysate suspension can be carried out to give 70–95% of the SO_4^{2-} in a weak acid fraction containing ca. 20–25 wt% free sulfuric acid, the remaining sulfate (5–30%) is highly diluted with wash-water.

In the past it has been common practice to discharge the waste acid directly into the open sea or coastal waters. For a long time the weak acid problem has been the subject of public discussion and criticism. As a result the European Community has decided to stop the discharge of weak acid into open waters until 1993.

The European titanium dioxide producers have developed different effluent treatment processes to meet the environmental requirements [2.47]. The most important processes are the precipitation of gypsum (CaSO_4) from the weak acid [2.48] and the concentration and recovery of the free and bound acid.

In the gypsum process the acid effluent is treated in a first stage with fine divided calcium carbonate (CaCO_3) to precipitate white gypsum. After filtering off, washing and drying the white gypsum is used for the manufacturing of plaster boards. In a second stage the remaining metal sulfates in the filtrate are precipitated by treating with calcium hydroxide as metal hydroxides and further gypsum. This mixture, the red gypsum, can be used e.g. for landfill.

In the recycling process both the free and the bound sulfuric acid (as metal sulfates) can be recovered from the weak acid in the calcination furnace (Fig. 17, k) and in metal sulfate calcination (Fig. 18). The process consists of two stages:

- 1) Concentration and recovery of the free acid by evaporation
- 2) Thermal decomposition of the metal sulfates and production of sulfuric acid from the resulting sulfur dioxide

As a result of energy requirements only acid containing $>20\%$ H_2SO_4 can be economically recovered by evaporation. The weak acid is concentrated from ca. 20–25% to ca. 28% with minimum heat (i.e., energy) consumption, e.g., by using waste heat from sulfuric acid produced by the contact process [2.49], or from the waste gases from the calcination kilns used in TiO_2 production [2.50] (Fig. 18).

Following preliminary evaporation, further concentration is carried out in multi-effect vacuum evaporators. Since the water vapor pressure decreases strongly as the H_2SO_4 concentration increases, in general only two-stage evaporation can effectively exploit the water vapor as a heating medium. Evaporation produces a suspension of metal sulfates in 60–70% sulfuric acid (stage 1 in Fig. 17). The suspension is cooled to 40–60°C in a series of stirred tanks (stage 2, d) [2.51], giving a product with good filtering properties and an acid of suitable quality for recycling to the digestion process. Filtration (stage 3, e) is usually carried out with pressure filters [2.52] because they give a filter cake with an extremely low residual liquid content.

The concentration of the acid recycled to the digestion process depends on the quality of the titanium-containing raw material. For raw materials with a high titanium content, the 65–70% sulfuric acid separated from the metal sulfates must be further concentrated to give 80–87% acid (stage 5).

Concentration can be carried out in steam-heated vacuum evaporators, or by using the heat from the TiO_2 calcination kilns [2.53]. Cooling the acid obtained after this concentration process yields a suspension of metal sulfates that can be directly used for digestion of the raw material. The metal sulfates recovered from the sulfuric acid in stage 3 are moist because they contain 65–70% sulfuric acid; they therefore have no direct use. They can be converted to a disposable material by reaction with calcium compounds [2.54]. Thermal decomposition of the metal sulfates to form the metal oxides, sulfur dioxide, water, and oxygen is energy intensive, but is advantageous from the ecological point of view. The energy requirement is ca. $4 \times 10^9 \text{ J}$ per tonne of filter cake. Thermal decomposition is carried out at 850–1100°C in a fluidized-bed furnace (stage 6). The energy is supplied by coal, pyrites, or sulfur. The sulfur dioxide produced by the thermal decomposition is purified by the usual methods, dried, and converted into sulfuric acid or oleum. This pure acid or oleum is mixed with the recovered sulfuric acid and used in the digestion process.

The metal oxides produced by thermal decomposition contain all the elements initially present in the raw material apart from the titanium which has been convert-

2.1. Titanium Dioxide 61

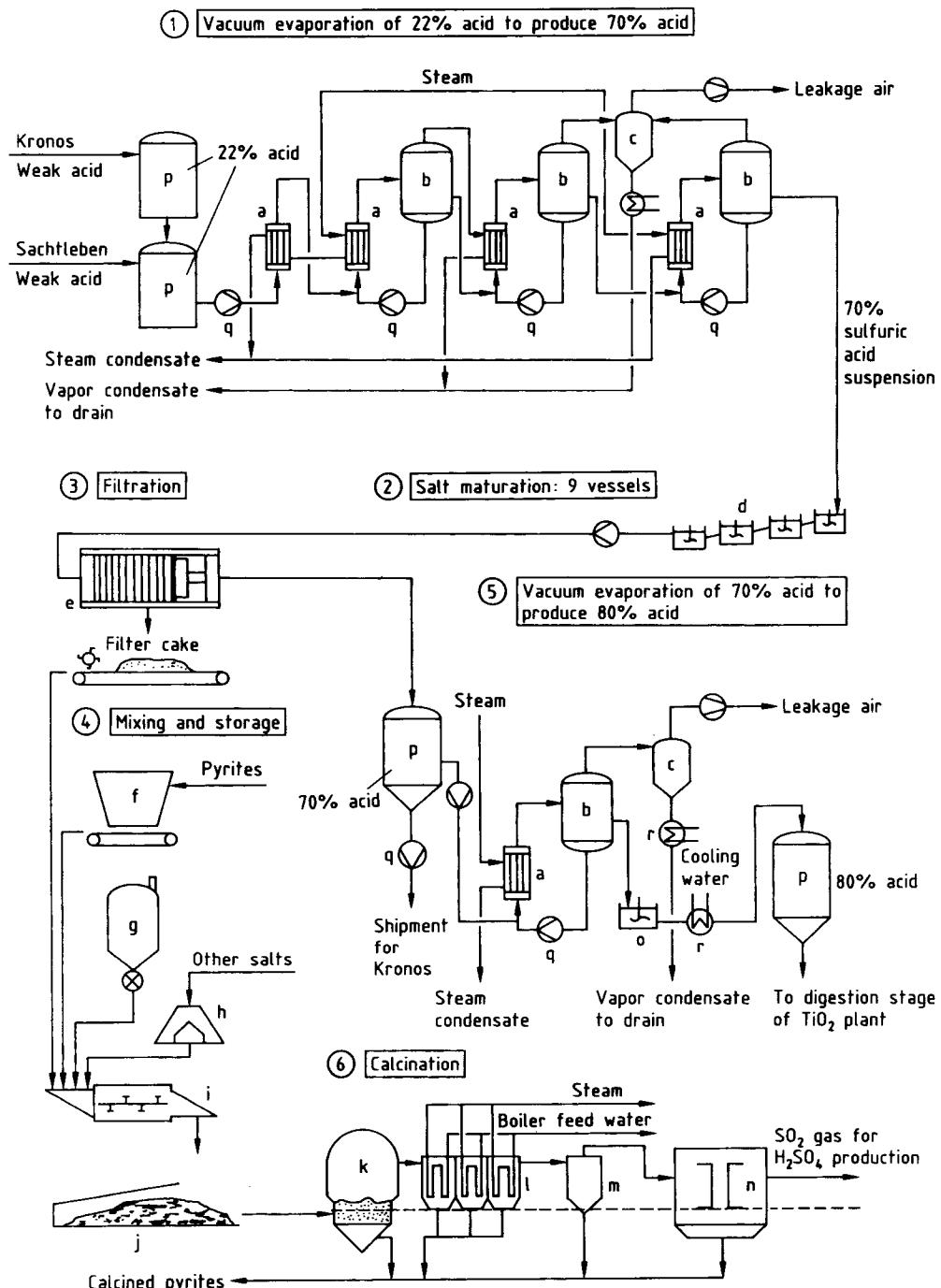


Figure 17. Weak acid recovery plant used by Sachtleben Chemie (based on know-how of Bayer AG)

a) Heat exchanger; b) Evaporator; c) Injection condenser; d) Stirred salt maturing vessels; e) Filter press; f) Bunker for pyrites; g) Coal silo; h) Bunker; i) Mixing screw unit; j) Covered store for mixed filter cake; k) Calcination furnace; l) Waste-heat boiler; m) Cyclone; n) Electrostatic precipitator; o) Stirred tank; p) Storage tank; q) Pump; r) Cooler

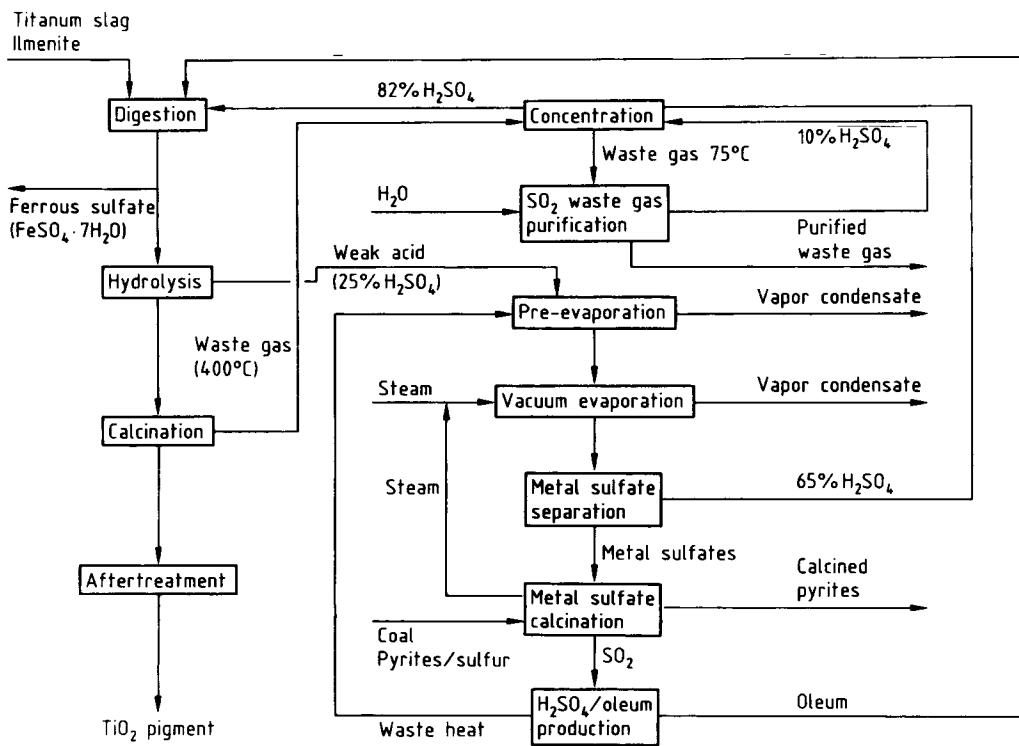


Figure 18. Waste heat recovery and sulfuric acid recycling during weak acid treatment (Bayer AG)

ed into pigment. The mixture of metal oxides, mainly iron oxide, can be used as an iron compound in the construction industry.

The continually increasing demand for environmentally friendly industrial processes has also led to the development of techniques for recycling of the remaining 5–30% sulfate contained in the acidic wash water [2.55]. In modern processes, up to 99% of sulfuric acid can be recovered and reused in production. In the *chloride process*, wastewater problems arise if the raw material contains < 90% TiO_2 . The metal chloride by products are sometimes disposed of in solution by the “deep well” method (e.g., at Du Pont). The metal chloride solutions are pumped via deep boreholes into porous geological strata. Special geological formations are necessary to avoid contamination of the groundwater by impurities.

Increasing restrictions also apply to the chloride process, so that efforts are continually being made to use the iron chloride byproduct, e.g., in water treatment and as a flocculation agent [2.56]. Another process for treating metal chlorides with cement and alkaline compounds to produce rock-like aggregates for road building is described in [2.57].

Waste Gas Problems. The gases produced in the calcination kiln are cooled in a heat exchanger, and entrained pigment is removed, washed, and recycled to the process. The SO_2 and SO_3 formed during calcination are then scrubbed from the gases to form dilute sulfuric acid which is recycled.

2.1.4. Economic Aspects

The burning of $TiCl_4$ with oxygen or the calcination of TiO_2 hydrolysates produces either anatase or rutile pigments, depending on the doping and lattice stabilization. They are marketed directly or after being coated with oxides or hydroxides of various elements. Different treatments are necessary depending on the field of application, and all major pigment producers have a large number of pigment grades. Product groups are listed in Table 15. Pigments of all grades are available with or without organic treatment. Over 400 different TiO_2 pigment grades are currently on the market. Table 16 gives the capacities and processes of the most important pigment producers.

A considerable increase of capacity is planned by debottlenecking and building new plants. Pigment plant capacity is forecast to grow to 5.2×10^6 t in 2005 [2.58].

Powdered TiO_2 pigments are usually supplied in 25 kg sacks (50 lbs, USA) or in large bags containing 0.5–1 t pigment. Aqueous suspensions with solids contents of 68–75% are also available and have great advantages as regards the distribution and metering of the pigment in aqueous systems. The dust formation that occurs with dry pigment is also avoided. With the development of products with improved flow properties and modern pneumatic delivery technology, supply in silo wagons is becoming increasingly important.

2.1.5. Pigment Properties

The pigment properties are extremely important when TiO_2 is used as a white pigment; they include lightening power, hiding power, lightness, hue, gloss formation, gloss haze, dispersibility, lightfastness, and weather resistance. These properties are a function of chemical purity, lattice stabilization, particle size and size distribution, and the coating produced by aftertreatment. They also depend on the medium and cannot generally be accurately described in scientific terms. Some of the important properties of TiO_2 pigments are described below.

Scattering Power. The refractive indices of rutile and anatase are very high (2.70 and 2.55, respectively). Even after incorporation in a wide range of binders, they lie

Table 15. Classification of TiO_2 pigments according to composition (DIN 55912, sheet 1, issue 07.85, ISO 591–1977)

Pigment	Class	TiO_2 (min.), wt %	Water-soluble salts, wt %	Volatiles (max.), wt %
Anatase (Type A)	A 1	98	0.6	0.5
	A 2	92	0.5	0.8
Rutile (Type R)	R 1	97	0.6	0.5
	R 2	90	0.5	to be agreed
	R 3	80	0.7	to be agreed

Table 16. World TiO₂ pigment producers (1995)

Country	Company	Location	Capacity, 10 ³ t/a		
			Chloride	Sulfate	Total
United States	Du Pont	New Johnsonville	305		305
		De Lisle	245		245
		Edge Moore	127		127
		Antioch	38		38
		Baltimore	50	66	116
	SCM Corporation	Ashtabula	165		165
		Kemira Oy	91	54	145
		Kerr McGee Corporation	130		130
		Tioxide	50		50
		NL Chemical Incorporated	50		50
Canada	NL Chemicals Incorporated	Varennes	50	36	86
Brazil	Titanio do Brasil/Bayer	Salvador		55	55
Mexico	Du Pont	Tampico	80		80
<i>Total, America</i>					1592
Germany	Kronos Titan	Leverkusen	80	35	115
	NL Chemicals	Nordenham		60	60
	Bayer	Krefeld-Uerdingen		105	105
	Sachtleben Chemie, Metallgesellschaft	Duisburg-Homberg		80	80
	Tioxide UK	Grimsby		100	100
	Tioxide UK	Greatham	80		80
	SCM Chemicals	Stallingborough	109	10	119
	Thann et Mulhouse (Rhône-Poulenc)		Le Havre	95	95
		Thann		30	30
	Tioxide France	Calais		100	100
Finland	Kemira Oy	Pori		90	90
Italy	Tioxide Italia	Scarlino		80	80
Belgium	Kronos Titan	Langenbrügge	50		50
	Bayer	Antwerpen		33	33
	Tioxide Espan.	Huelva		80	80
Netherlands	Kemira	Botlek	45		45
Norway	Kronos Titan	Fredrikstad		32	32
<i>Total, Western Europe</i>					1294

Russia	Lakokraska	Chelyabinsk	10	10	
Ukraine	Lakokraska	Armyansk	80	80	
	Agrokhim	Sumy	40	40	
Poland	Zachem	Police	36	36	
Yugoslavia	Cinkarna	Celje	25	25	
Czechoslovakia	Precheza	Prerov	25	25	
<i>Total, Eastern Europe</i>					<i>216</i>
Republic of South Africa	SA Tioxide	Umbogintwini	38	38	
<i>Total Africa</i>					<i>38</i>
Australia	SCM Chemical	Kemerton	79	79	
	Tioxide Australia	Burnie		35	35
	Kerr Mc Gee Corporation	Kwinana	64		64
<i>Total, Australia</i>					<i>178</i>
Japan	Ishihara Sangyo Kaisha	Yokkaichi	55	100	155
	Tayca	Saidaiji		60	60
	Sakai Chemical	Onahama		43	43
	Furukawa Mining	Osaka		23	23
	Fuji Titanium	Kobe		16	16
	Titan Kogyo	Ube		17	17
	Tohoku Chemical	Akita		30	30
<i>Total, Japan</i>					<i>344</i>
India	Kerala Minerals & Metals	Kerala	22		22
	Travancore Titanium	Trivandrum		13	13
South Korea	Hankook Titanium	Incheon		36	36
Taiwan	China Metal & Chemicals	Chin Shin		10	10
	Du Pont	Kuan Yin	60		60
Malaysia	Tioxide	Terengganu		50	50
S. Arabia	Christal	Yanbu	55		55
<i>Total, Far East</i>					<i>246</i>
<i>(excluding Japan)</i>					
<i>Total world capacity</i>			2080	1828	3908
					65

in the range between 1.33 (water) and 1.73 (polyester fibers). The scattering power depends on the particle size, and for TiO_2 is at its maximum at a particle size of 0.2 μm (Mie's theory) [1.26]. The scattering power also depends on the wavelength; TiO_2 pigment particles with a size $\leq 0.2 \mu\text{m}$ scatter light of shorter wavelengths more strongly and therefore show a slight blue tinge, while larger particles have a yellow tone.

Hue. The whiteness (lightness and hue) of TiO_2 pigments depends primarily on the crystalline modification, the purity, and the particle size of the TiO_2 (see above). As the absorption band (385 nm) of anatase pigments is shifted into the UV region, compared with rutile pigments they have less yellow undertone. Any transition elements present in the crystal structure have an adverse effect on the whiteness, so manufacturing conditions are of the greatest importance. Thus, pigments produced by the chloride process (which includes distillative purification of TiCl_4 before the combustion stage) have a higher color purity and very high lightness values.

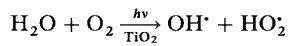
Dispersion. Good disintegration and dispersion of the TiO_2 pigments in the medium are necessary to obtain high gloss and low gloss haze. These requirements are satisfied by intensive grinding and by coating the pigment surface with organic compounds. The compounds used for this surface treatment depend on the field of application (see Section 2.1.3.4).

Lightfastness and Weather Resistance. Weathering of paints and coatings containing TiO_2 leads to pigment chalking [2.59]. If weathering occurs in the absence of oxygen, or in binders with low permeability to oxygen (e.g., in melamine-formaldehyde resins), no chalking is observed, but graying takes place, which decreases on exposure to air. Graying is greatly reduced in the absence of water. Both effects are more severe with anatase pigments. Empirical stabilization processes have been developed by pigment producers, e.g., doping with zinc or aluminum prior to calcination.

According to modern theories, impairment of the lightfastness and weather resistance of TiO_2 pigments proceeds according to the following cycle [2.60]:

- 1) Molecules of water are bound to the TiO_2 surface, forming hydroxyl groups on the surface.
- 2) Absorption of light of short wavelength (anatase $< 385 \text{ nm}$, rutile $< 415 \text{ nm}$) occurs, producing an electron and an electron defect or "hole" (exciton) in the crystal lattice which migrate to the surface of the pigment.
- 3) At the surface of the pigment, an OH^- ion is oxidized to an OH^\cdot radical by an electron "hole". The OH^\cdot radical is then desorbed and can oxidatively break down the binder. A Ti^{3+} ion is simultaneously produced by reduction of Ti^{4+} with the remaining electron of the exciton.
- 4) The Ti^{3+} ion can be oxidized by adsorbed oxygen with formation of an O_2^- ion. The latter reacts with H^+ and is converted into an HO_2^\cdot radical.
- 5) The cycle ends with the binding of water to the regenerated TiO_2 surface.

The chalking process can be regarded as the reaction of water and oxygen to form OH^\cdot and HO_2^\cdot radicals under the influence of shortwave radiation and the catalytic activity of the TiO_2 surface:



The enthalpy requirement for this reaction (312 kJ/mol) is provided by radiation of wavelength 385 nm. The cycle (1)–(5) is broken by excluding air or water. If oxygen is excluded or a binder is chosen in which the diffusion of oxygen is rate determining, a concentration of Ti^{3+} ions builds up. Graying then takes place, but this decreases with gradual exposure to oxygen. If water is excluded, rehydration and formation of surface hydroxyl groups do not take place; breakdown of the binder therefore ceases. Despite this photochemical breakdown of the binder, treated rutile pigments are used to stabilize many binders. This is because nonpigmented coatings are degraded by exposure to light and weathering; the added TiO_2 pigments prevent light from penetrating the deeper layers of the coating film and thus inhibit breakdown of the binder. High-quality TiO_2 pigments must satisfy stringent requirements with respect to weather resistance. They must withstand the severe climatic conditions of the Florida test, resisting a two-year exposure without appreciable chalking or deterioration of gloss.

2.1.6. Analysis

The crystal structure of the pigments is determined by X-ray analysis which is sensitive enough to determine 0.3–0.5% anatase in the presence of 99.7–99.5% rutile. For standards, see Table 1 (Titanium dioxide pigments; “Methods of analysis” and “Specification”).

A qualitative test for TiO_2 is a blue-violet coloration of beads of microcosmic salt ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$), or a yellow-orange coloration produced when hydrogen peroxide is added to a test solution in hot, concentrated sulfuric acid containing ammonium sulfate. For quantitative determination, the pigment is dissolved or digested in sulfuric acid and the solution is reduced to Ti^{3+} with cadmium, zinc, or aluminum. The Ti^{3+} ions are then usually titrated with a standard solution of iron(III) ammonium sulfate solution, with potassium rhodanide as an indicator, or using potentiometric end point determination.

Impurities can be determined by wet analysis, X-ray fluorescence, or spectrographic analysis (e.g., atomic absorption).

Typical analysis figures for an untreated rutile pigment are TiO_2 99.4%, K_2O 0.24%, P_2O_5 0.21%, Fe_2O_3 40 ppm, Sb_2O_3 24 ppm, Al_2O_3 20 ppm, Mg 5 ppm, Zn 3 ppm, Cr 2 ppm, Mn, Cu, Hg, Cd, Co, Ni, Se, Sn, Ag <1 ppm.

2.1.7. Uses of Pigmentary TiO_2

Titanium dioxide is used universally, having almost completely replaced other white pigments. Consumption figures for 1996 are given in Table 17 [2.61]. The greatest annual increase in use has been for coloring plastics (5.5%), followed by the coloring of paper (3.0%). Geographically, the increase in consumption of TiO_2 has been the greatest in Asia (see Table 18).

Table 17. Consumption of TiO₂ pigments in 1996 [2.61]

Use	World total	
	[10 ³ t]	[%]
Coatings	1988	59
Paper	424	13
Plastics	686	20
Other	286	8
Total	3384	100

Table 18. Predicted percentage annual growth rates for use of TiO₂ (1993–2000) [2.3]

End use	United States	Europe, Middle East, Africa	Asia and Pacific	World total
Coatings	3,4	2,0	5,0	2,5
Paper	2,0	4,0	4,0	3,0
Plastics	4,5	5,0	10,0	5,5
Total	3,0	2,5	6,5	3,3

Paints and coatings account for the largest volume of TiO₂ production. The presence of the pigment enables the protective potential of the coating material to be fully exploited. As a result of continuing developments in TiO₂ pigments, coatings only a few micrometers thick fully cover the substrate. Commercially available pigments permit paint manufacture with simple dispersion equipment, such as disk dissolvers. Organic treatment (see Section 2.1.3.4) prior to steam jet micronization yields pigments with improved gloss properties and reduced gloss haze for use in stoving enamels. Sedimentation does not occur when these products are stored, and they possess good lightfastness and weather resistance.

Printing Inks. Modern printing processes operate at coating thicknesses of < 10 µm, and therefore require the finest possible TiO₂ pigments. These very low film thicknesses are only possible with TiO₂ pigments that have a lightening (reducing) power seven times that of lithopone. Because of its neutral hue, TiO₂ is especially suitable for lightening (reducing) colored pigments.

Plastics. Titanium dioxide is used to color durable and non durable goods like toys, appliances, automobiles, furniture and packaging films. Furthermore, TiO₂ pigments absorb UV radiation with a wavelength < 415 nm and thus protect the pigmented goods from these harmful rays.

Fibers. Titanium dioxide pigments give a matt appearance to synthetic fibers, eliminating the greasy appearance caused by their translucent properties. Anatase pigments are used for this because their abrasive effect on the spinning operation is about one quarter that of the rutile pigments. The poor lightfastness of anatase pigments in polyamide fibers can be improved by treatment with manganese or vanadium phosphate.

Paper. In Europe, fillers such as kaolin, chalk, or talc are preferred as brightening agents and opacifiers in paper manufacture. Titanium dioxide pigments are suitable for very white paper that has to be opaque even when very thin (air mail or thin printing paper). The TiO_2 can be incorporated into the body of the paper or applied as a coating to give a superior quality ("art" paper).

Laminated papers are usually colored with extremely lightfast rutile pigments before being impregnated with melamine-urea resin for use as decorative layers or films.

Other areas of application for TiO_2 pigments include the enamel and ceramic industries, the manufacture of white cement, and the coloring of rubber and linoleum.

Titanium dioxide pigments are also used as UV absorbers in sunscreen products, soaps, cosmetic powders, creams, toothpaste, cigar wrappers, and in the cosmetics industry. Their most important properties are their lack of toxicity, compatibility with skin and mucous membranes, and good dispersibility in organic and inorganic solutions and binders.

Electrically-conducting TiO_2 pigments have been produced by an aftertreatment to give a coating of mixed oxides of indium and tin, or antimony and tin [2.62]. These pigments are applied to fibers used in photosensitive papers for electrophotography, and for the production of antistatic plastics.

2.1.8. Uses of Nonpigmentary TiO_2

A number of industrial products require TiO_2 starting materials with well-defined properties for a specific application. Some of the most important of these grades of titanium dioxide are those with a high specific surface area, a small particle size, and very high reactivity. Stringent requirements often exist regarding purity and property consistency. The most important applications for nonpigmentary TiO_2 are vitreous enamels, glass and glass ceramics, electroceramics, catalysts and catalyst supports, welding fluxes, colored pigments, electrical conductors, chemical intermediates like potassium fluorotitanate, structural ceramics, UV-absorbers and refractory coatings [2.63]. The annual growth rate in these markets is expected to be a few per cent.

Electroceramics. Titanates like barium, strontium, calcium and lead titanate prepared from finely divided, high-purity TiO_2 hydrolysates are used in capacitors, PTC-resistors and piezoelectric materials. The specifications of the TiO_2 starting materials with respect to purity, reactivity, and sintering properties are expected to become more stringent. The market is estimated to be several thousand of tonnes a year as TiO_2 . A strong annual growth is expected.

Catalysts. Titania is an active catalyst for different reactions, inorganic and organic, thermal and photochemical. It may be self-supported, or it may be supported on

other material. For catalysis it is usually doped with other elements in order to enhance the desired effect.

The most important application for TiO_2 is the removal of nitrogen oxides from waste gases from power stations and industry. The nitrogen oxides in the waste gas react with ammonia in the presence of oxygen over the catalyst to produce nitrogen and water (SCR, Selective Catalytic Reduction) [2.64]. The world market for SCR catalysts is believed to be several thousand tonnes a year as TiO_2 . In addition to TiO_2 the catalysts usually contain ca. 10 wt % tungsten oxide and 1 wt % V_2O_5 , and are extruded into a honeycomb shape or supported in thin layers on metal sheets. The TiO_2 has high specifications with respect to purity, particle size, and porosity to ensure that the desired catalytic activity is obtained.

An increasing demand is expected for the removal of nitrogen oxides from waste gases from stationary and instationary diesel engines for e.g. emergency plants, ships and trucks. Another application is the combined removal of nitrogen oxides and dioxines from waste gases of refuse disposal plants [2.65].

Mixed Metal Oxide Pigments. The starting material is a TiO_2 hydrolysate, which is calcined with oxides of transition metals to form chromium rutile or nickel rutile pigments (see Section 3.1.3.1).

UV Absorption. Nanostructured TiO_2 particles (5–50 nm particle size) are used as sunscreen filter in the cosmetic industry for skin protection. Nanosized TiO_2 is an effective UV-absorber against UV-B (280–320 nm) and UV-A rays (320–400 nm). Because of its small particle size it appears transparent [2.66]. Intensive research work is in progress worldwide aimed at utilizing the photoactivity of TiO_2 . Titanium dioxide catalyzes the decomposition of organic compounds in wastewater [2.67]; water is decomposed into hydrogen and oxygen in the presence of sunlight.

2.1.9. Toxicology

Titanium dioxide is highly stable and is regarded as completely nontoxic. Investigations on animals which have been fed TiO_2 over a long period give no indication of titanium uptake [2.68]. Absorption of finely divided TiO_2 pigments in the lungs does not have any carcinogenic effect [2.69].

2.2. Zinc Sulfide Pigments [2.70]–[2.72]

White pigments based on zinc sulfide were first developed and patented in 1850 in France. Although they are still of economic importance, they have continually lost market volume since the early 1950s when titanium dioxide was introduced. Only one modern production installation for zinc sulfide pigments still exists in the mar-

United States Patent Office

3,009,772

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1

PROCESS FOR THE PURIFICATION OF
TITANIUM TETRACHLORIDE

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company
No Drawing. Filed Sept. 20, 1957, Ser. No. 685,084
Claims priority, application Great Britain Sept. 25, 1956
10 Claims. (Cl. 23—87)

It is known to purify liquid titanium tetrachloride containing vanadium as an impurity by heating the tetrachloride with a small proportion of an organic material (see, for example, United States specifications Nos. 2,230,538 and 2,592,021 and British specification No. 656,098). The organic materials used are those which are capable of undergoing carbonisation, probably preceded by polymerisation, in the presence of the titanium tetrachloride under the conditions used, for example, when the impure titanium tetrachloride and the organic material are heated at or above the boiling point of titanium tetrachloride. The vanadium impurity and, when present, certain other metallic impurities, for example, iron and chromium, are taken up by the solid products of carbonisation, and are removed by separating the solid carbonisation products from the liquid titanium tetrachloride, for example, by distilling off the tetrachloride or by filtration or centrifuging.

Organic materials that carbonise slowly, for example, saturated aliphatic hydrocarbons, such as liquid paraffin, are satisfactory as purifying agents only at temperatures above the boiling point of titanium tetrachloride or if a mixture of liquid titanium tetrachloride and the organic material is boiled under reflux for several hours. More readily carbonisable materials, such as vegetable oils or mineral oils containing unsaturated hydrocarbons, have a greater purifying power, but they tend to contaminate the purified product with organic substances which subsequently impart a dark colour to the product when it is distilled. Such contamination is undesirable for some purposes for which the titanium tetrachloride is to be used, for example, for the manufacture of titanium metal.

The present invention provides a process for the purification of titanium tetrachloride containing vanadium as an impurity, wherein the impure liquid titanium tetrachloride is heated with a small proportion of a carbonisable organic material in the presence of a proportion of finely divided metallic sodium amounting to about 5 to 50 percent calculated on the weight of the organic material to bring about carbonisation of the organic material, and the purified titanium tetrachloride is separated from the solid carbonisation products containing the impurities.

The presence of the finely divided metallic sodium has the effect of accelerating the purifying action of the organic material, and therefore enables the throughput of titanium tetrachloride to be purified to be increased and/or the proportion of the organic material, and consequently the amount of waste residue for disposal, to be decreased. Moreover, the extent to which the purified titanium tetrachloride is contaminated with organic matter can be reduced by using organic materials that carbonise slowly and without the long reaction periods that such materials normally require. Furthermore, the quantity of certain other impurities in the final product, such as free chlorine and hydrogen chloride, is less since the sodium reacts with them.

The temperature at which the titanium tetrachloride is heated with the organic material and the metallic sodium is preferably at least 100° C. The heating may be carried out under atmospheric pressure or a higher or

2

lower pressure. Advantageously, the titanium tetrachloride is heated in the liquid state with the organic material and the metallic sodium under atmospheric pressure at a temperature within the range of 100° C. up to the boiling temperature of titanium tetrachloride, viz. 136° C. A convenient method is to boil the titanium tetrachloride under reflux in the presence of the organic material and metallic sodium.

Any organic material capable of undergoing carbonisation when heated in liquid titanium tetrachloride may be used, for example, the materials used in the known processes referred to above. The proportion of the organic material is advantageously within the range of 0.1 to 1.0 percent calculated on the weight of the titanium tetrachloride to be purified. The organic material is advantageously one which, when used alone, is slowly carbonisable, since such materials are generally less costly than the more reactive materials and so greater benefit is derived from the accelerating action of the finely divided metallic sodium. As slowly carbonisable materials there are meant carbonisable saturated or unsaturated organic materials having an iodine value not exceeding 25. Such organic materials are mineral oils, such as crude petroleum oil or petroleum distillates, which are saturated or have a content of unsaturated compounds such that their iodine value does not exceed 25. Alternatively, there may be used vegetable or animal oils, fats or waxes, which do not exceed the aforesaid degree of unsaturation. The iodine values referred to herein are those determined by the iodine monochloride method described in the British Pharmacopoeia, 1953, pages 754—755.

It has been found, for example, that the presence of finely dispersed metallic sodium in a mineral oil in a proportion amounting to 20 percent of the weight of the oil decreases the period of the purification treatment by at least 50 percent as compared with the period required for purification with the mineral oil alone.

The finely divided metallic sodium preferably has a particle size not exceeding 150 microns. It is advantageously used in the form of a dispersion in an organic liquid. Such dispersions and methods of preparing them are known, see, for example, United States specifications Nos. 2,394,608, 2,487,333 and 2,487,334. When the organic dispersing medium is capable of undergoing carbonisation when heated in liquid titanium tetrachloride, as in the case of a mineral oil, it may also serve as the carbonisable organic material used in the present process.

Titanium tetrachloride which has been purified by the process of this invention is very suitable for the manufacture of titanium dioxide or metallic titanium or organic compounds of titanium, and as a catalyst in various processes for polymerising organic compounds.

The following example illustrates the invention: 100 parts by weight of crude liquid titanium tetrachloride containing 0.052 percent of vanadium (calculated as V_2O_5) were heated at the boil under reflux with 0.14 part by weight of the mineral lubricating oil having an iodine number of 12, and known in commerce as "Vitreo 69," in which oil 0.04 part by weight of metallic sodium had been finely dispersed in the form of particles of less than 150 microns by agitating molten sodium with the hot oil by means of a high speed stirring device. The refluxing was continued until vanadium could no longer be detected in the vapour above the boiling liquid. The titanium tetrachloride was then distilled off and collected. The purified product contained less than 2.5×10^{-5} percent of vanadium (calculated as V_2O_5). The refluxing period was 50 minutes.

The above procedure was repeated without the addition of the sodium, and in this case a refluxing period

of 135 minutes was required to achieve the same degree of purity.

The procedure described in the first paragraph of the above example was repeated without the addition of the lubricating oil, and with 0.04 part by weight of metallic sodium alone. The metallic sodium was used in the form of a coating on the particles of a dry inert powder. The purification was not complete after refluxing for five hours.

It was also found that traces of impurities, such as 10 chlorine and hydrogen chloride, which were present in some samples of titanium tetrachloride purified by refluxing with the lubricating oil alone, were not present in the samples purified in the presence of the dispersion of sodium in the mineral oil.

I claim:

1. A process for the purification of titanium tetrachloride containing vanadium as an impurity, which comprises heating the impure liquid titanium tetrachloride with a proportion of an organic material carbonizable under process conditions within the range of 0.1 to 1.0 percent calculated on the weight of the impure titanium tetrachloride in contact with a proportion of finely divided metallic sodium within the range of about 5 to 50 percent calculated on the weight of the organic material, such heating being sufficient to bring about carbonization of the organic material while maintaining a pressure sufficient to maintain the titanium tetrachloride in liquid state, and separating the purified titanium tetrachloride from the solid carbonization products.

2. A process as claimed in claim 1, wherein the impure titanium tetrachloride is heated with the organic material and the metallic sodium at a temperature of at least 100° C.

3. A process as claimed in claim 1, wherein the impure titanium tetrachloride is heated with the organic material and the metallic sodium under atmospheric pressure at a temperature within the range of 100° C. to 136° C.

4. A process as claimed in claim 1, wherein the finely divided metallic sodium has a particles size not exceeding 150 microns.

5. A process as claimed in claim 1, wherein the impure titanium tetrachloride is heated with the carbonizable organic material in the presence of a dispersion of the finely divided metallic sodium in an organic liquid.

6. A process as claimed in claim 1, wherein the car-

bonizable organic material is a carbonizable organic liquid containing the finely divided metallic sodium dispersed therein.

7. A process as claimed in claim 1, wherein the carbonizable material has an iodine value not exceeding 25.

8. A process as claimed in claim 1, wherein the carbonizable organic material is selected from the group consisting of vegetable and animal oils, fats and waxes having an iodine value not exceeding 25.

9. A process as claimed in claim 1, wherein the carbonizable organic material is a mineral oil having an iodine value not exceeding 25.

10. A process for the purification of titanium tetrachloride containing vanadium as an impurity, which comprises heating the impure liquid titanium tetrachloride under atmospheric pressure at a temperature within the range of 100° C. to 136° C. with a mineral oil having an iodine value not exceeding 25 which is present in a proportion within the range of 0.1 to 1.0 percent calculated on the weight of the impure titanium tetrachloride and contains dispersed therein a proportion of about 5 to 50 percent calculated on the weight of the mineral oil of finely divided metallic sodium having a particle size not exceeding 150 microns to bring about carbonization of the mineral oil, and separating the purified titanium tetrachloride from the solid carbonization products.

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United States Patent [19]

Winter et al.

[11] 3,963,585

[45] June 15, 1976

[54] DISTILLATION OF TITANIUM TETRACHLORIDE IN SOLUTION WITH SELECTED AMINES

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[73] Assignee: Bayer Aktiengesellschaft, Leverkusen, Germany

[22] Filed: May 1, 1974

[21] Appl. No.: 465,954

[30] Foreign Application Priority Data

May 22, 1973 Germany..... 2325924

[52] U.S. Cl. 203/38; 203/59; 203/32; 423/67; 423/81; 423/264; 423/492; 260/429 R

[51] Int. Cl. B01D 3/34

[58] Field of Search 203/28, 32, 38, 50, 203/57, 59; 423/491, 492; 106/73.3; 260/429 R

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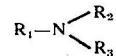
Primary Examiner—Norman Yudkoff

Assistant Examiner—Frank Sever

Attorney, Agent, or Firm—Burgess, Dinklage & Sprung

[57] ABSTRACT

In the purification of impure titanium tetrachloride comprising adding an agent to said titanium tetrachloride and thereafter distilling off purified titanium tetrachloride while leaving the impurity in the distillation residue, the improvement which comprises employing as said agent at least one amine of the formula



in which

R_1 and R_2 each independently is hydrogen, alkyl or alkenyl of up to 6 carbon atoms, cycloalkyl of 5 to 7 carbon atoms, or aryl, and

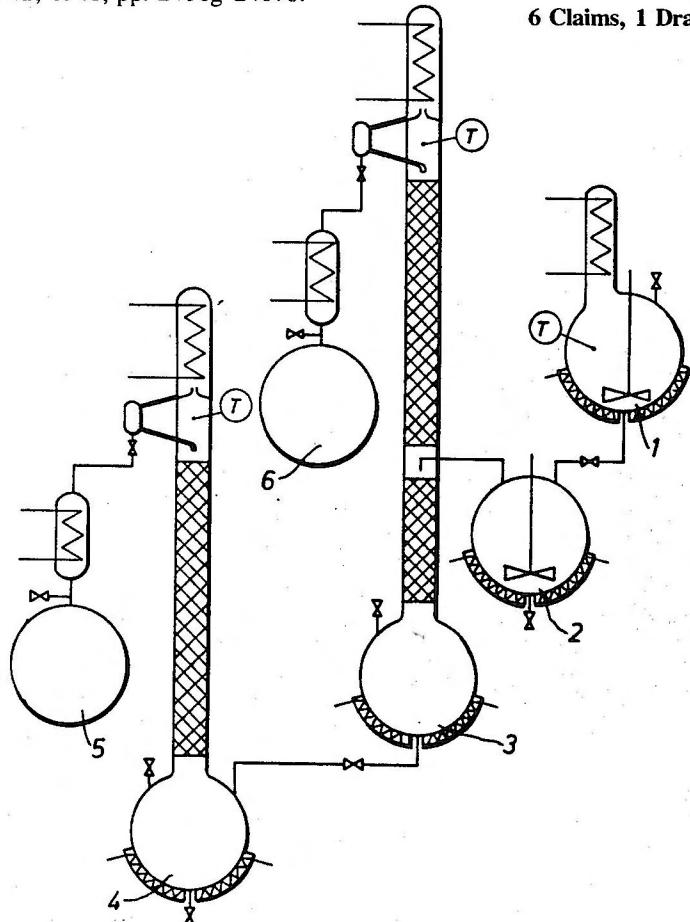
R_3 is cycloalkyl of 5 to 7 ring carbon atoms, or aryl, or

R_2 together with R_3 is butylene, pentylene or hexylene, in which event

R_1 is hydrogen, alkyl of up to 6 carbon atoms or aryl.

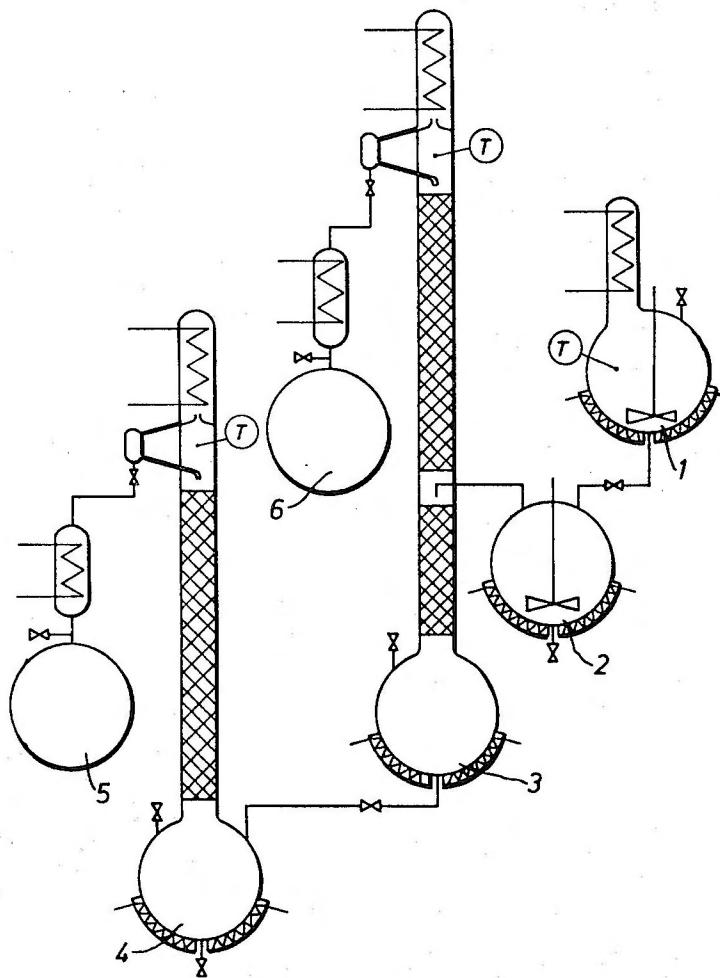
The preferred agents are aniline, cyclohexylamine, N,N-dimethyl-aniline, diphenylamine, 2,3-dimethyl-aniline and 2,6-dimethyl-aniline. The process serves to remove vanadium impurities.

6 Claims, 1 Drawing Figure



U.S. Patent June 15, 1976

3,963,585



DISTILLATION OF TITANIUM TETRACHLORIDE IN SOLUTION WITH SELECTED AMINES

This invention relates to a process for the continuous or batch removal of vanadium compounds and other impurities from titanium tetrachloride, in which the $TiCl_4$ is heated in the presence of an organic compound which is able to react with vanadium chloride or vanadium oxychloride under normal pressure and at temperatures of up to $136^\circ C$. Amines have proved to be particularly effective in this respect. High reactivity is shown by amines which contain at least one optionally substituted cyclohexyl or phenyl radical.

Nowadays the so-called combustion process is also used for the production of white titanium dioxide pigments or optical oxides. In this process, $TiCl_4$ and oxygen are directly reacted at an elevated temperature to form titanium dioxide pigments. The $TiCl_4$ required for this reaction is obtained by the chloridizing decomposition of titanium-containing materials such as ilmenite, leucoxen or rutile, but unfortunately it is contaminated by a number of other chlorides (so-called crude $TiCl_4$). These other chlorides present in the $TiCl_4$ are predominantly the chlorides of iron, aluminum and silicon; also the chlorides and oxychlorides of vanadium.

It is absolutely essential to remove these impurities if pure white TiO_2 pigments are to be obtained. One method of purifying titanium tetrachloride is distillation. $TiCl_4$ boils at $136^\circ C$ under normal pressure and, for this reason, can be separated by distillation from most of its impurities, such as iron, aluminum and silicon. In this way it is possible to obtain a product referred to hereinafter as "commercial-grade titanium tetrachloride". Vanadium is normally present in this commercial-grade $TiCl_4$, in the form of $VOCl_3$ (b.p. $127^\circ C$) or VCl_4 (b.p. $154^\circ C$). Due to their similar boiling points, both of these compounds are extremely difficult to separate from titanium tetrachloride by distillation.

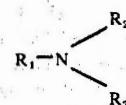
A number of proposals have already been put forward with a view to simplifying the complicated distillation process, almost all of which comprise converting the vanadium into a low oxidation stage and subsequently separating the $TiCl_4$ by distillation. For example, it is known that purification can be carried out with H_2S (German Offenlegungsschrift DOS No. 1,923,479); with animal and vegetable oils, fats, waxes, resins and soaps; with liquid, vapor or gaseous hydrocarbons, oils, fats, alcohols, ketones, organic acids, amines (Swiss Patent Specification No. 265,393 and No. 262,267; German Auslegeschrift DAS No. 1,289,839; No. 1,275,524 and No. 1,237,081; German Patent Specification No. 867,544; French Patent Specification No. 1,466,478 and No. 1,460,362), and with metals and metal salts (Belgian Patent Specification No. 539,078; German Offenlegungsschrift DOS No. 1,922,420; German Auslegeschrift DAS No. 1,271,693 and U.S. Pat. Nos. 2,915,364; 2,871,094; 2,754,255; 2,560,424; 2,555,361 and 2,530,735). Some idea of the necessary outlay involved can be derived from German Offenlegungsschrift DOS No. 2,135,250. In order to purify $TiCl_4$ having a vanadium content of 50 ppm, the $TiCl_4$ is boiled under reflux in the presence of benzene sulfenic acid dichloramide and metallic copper; The $TiCl_4$ which distills off still contains from 1 to 5 ppm of vanadium.

Additives which can readily be separated from the purified $TiCl_4$, either because they have a different boiling point or because they can be removed in the solid form together with the reduced vanadium compounds, are of particular advantage.

One particular elegant, although uneconomical, process comprises adding titanium subhalides such as $TiCl_3$. In cases where $TiCl_3$ is added, purified, colorless $TiCl_4$ can be distilled off after boiling for several hours (U.S. Pat. No. 2,178,685). Although the long reduction period for vanadium oxychloride is reduced by using $TiCl_3 \cdot 0.33 AlCl_3$ in accordance with application Ser. No. 347,584, filed Apr. 2, 1973, now pending, the high price of the cocrystallized $TiCl_3 \cdot 0.33 AlCl_3$ prevents this from being used on an industrial scale.

It is accordingly an object of the present invention to provide a simple, inexpensive process for purifying titanium tetrachloride.

These and other objects are realized in accordance with the present invention which involves purification of impure titanium tetrachloride by adding an agent thereto followed by distilling off purified titanium tetrachloride while leaving the impurity in the distillation residue. In accordance with the invention the added agent is an amine of the formula



in which

R_1 and R_2 each independently is hydrogen; aryl of 1 to 6 carbon atoms such as methyl, ethyl, isopropyl and hexyl; alkenyl of up to 6 carbon atoms such as vinyl and propenyl; cycloalkyl of 5 to 7 ring carbon atoms such as cyclohexyl; or aryl such as phenyl; R_3 is cycloalkyl of 5 to 7 ring carbon atoms such as cyclohexyl, or aryl such as phenyl, or together with the radical R_2 is butylene, pentylene or hexylene forming with the nitrogen atom a 5- to 7-membered heterocyclic ring in which event R_1 is hydrogen; alkyl of 1 to 6 carbon atoms such as methyl, ethyl, and isopropyl, or aryl such as phenyl; cyclohexyl and aryl radicals may optionally contain one or more other substituents, namely alkyl of 1 to 6 carbon atoms, for example methyl or ethyl, halogen, for example Cl or Br, amino groups, for example $-NH_2$ or $-N(CH_3)_2$, hydroxyalkyl groups, for example hydroxymethyl, and the like. Examples of compounds such as these include aniline, cyclohexylamine, N,N-dimethyl-aniline, diphenylamine, 2,3-dimethyl-aniline, 2,6-dimethyl-aniline, pyrrolidine and piperidine. It is particularly preferred to use aniline and/or piperidine.

These amines react rapidly with the vanadium chloride or oxychloride at a temperature from room temperature up to the boiling point of the titanium tetrachloride, e.g. about 25° to $136^\circ C$, preferably at a temperature of about 60° to $100^\circ C$, and for this reason they enable the titanium tetrachloride to be continuously purified. Although it is preferred to purify commercial-grade $TiCl_4$ in accordance with the invention, it is also possible to purify $TiCl_4$ which contains other impurities in addition to the vanadium chloride. Iron and aluminum chlorides, $SiCl_4$, $ZrCl_4$ or other chlorides are

harmless. Although the presence of elemental chlorine results in a corresponding increase in the consumption of the reduction component, it does allow the advantage of having no dechlorination stage. The amines used in accordance with the invention are so inexpensive that a somewhat higher demand due to the presence of Cl_2 can be readily accepted and this demand does not have any adverse effect upon the economy of the process according to the invention.

Nowadays titanium tetrachloride in its crystal-clear form is a prized starting product for a number of applications. Particular importance is attached to a crystal-clear light-stable TiCl_4 . Hitherto the production of a light-stable titanium tetrachloride has involved a special purification stage. Following addition of the compounds according to the invention, for example diphenylamine, a crystal-clear light-stable TiCl_4 can be continuously obtained from the crude product which is obtained during the chlorination of TiO_2 without any need for additional purification stages.

The purification process according to the invention can be carried out continuously or in batches, by adding a corresponding amine to the TiCl_4 to form a vanadium-free TiCl_4 after heating and distillation.

In cases where the process according to the invention is carried out continuously, crude TiCl_4 in the form in which it accumulates following separation of most of the solid impurities (for example FeCl_3) and an amine, optionally suspended or dissolved in crude TiCl_4 , are introduced into a distillation flask. During distillation the reduced vanadium compounds and the oxidized amine are enriched in the distillation flask until the residue has a solids content of about 10 to 40 % by weight. The residue is discharged continuously or in batches and concentrated by evaporation. About 50 % of the TiCl_4 which distills can be added to the purified distillate. The remainder is returned to the crude TiCl_4 and the solids recovered as the residue. This residue contains vanadium in enriched form and, for this reason, can be used for the production of vanadium compounds. Another considerable advantage of the process according to the invention is in the wide dosage range of the active amines which are used as reducing agent.

The quantities required for the reduction are between about 0.1 and 5 moles of amine, based on vanadium, or to between about 0.1 and 10% by weight of amine, based on crude TiCl_4 , depending upon the vanadium content. The amine is preferably used in a quantity of about 0.2 to 1.5% by weight. If a sufficient quantity of reducing agent is added, reduction of the VOCl_3 begins instantaneously at temperatures above 60° to 80°C in the case of most amines, and a colorless or lightly coloured distillate having a vanadium content of less than 10 ppm, generally less than 1 ppm of vanadium, is obtained.

The invention will be further described in the accompanying drawing wherein the single FIGURE is a schematic view of an apparatus for carrying out the process.

Referring now more particularly to the drawing, crude TiCl_4 is heated to 60°C in a three-necked flask 1 equipped with a stirrer and an additional outlet in its base. Diphenylamine, used as reducing agent, is added. The mixture is run continuously into an indirectly heated three-necked flask 2 equipped with a stirrer and bottom outlet acting as an evaporator. The temperature of this flask 2 is kept at 136°C so that pure TiCl_4 distills off continuously. When the solids have been concentrated to around 20% in the flask 2, 10% of the

suspension is removed, the TiCl_4 distilled off, added to the crude TiCl_4 and the residue discharged. From this crude TiCl_4 circuit, the vanadium-free TiCl_4 distilling off is continuously introduced at the center of a first column, the readily volatile constituents accumulating in the head of the column 6. The sump 3 of this first column consists of vanadium-free TiCl_4 which progressively turns very slightly yellow in color when diphenylamine is used as the reducing agent. The TiCl_4 flows from the sump of the column 3 into another indirectly heated flask 4 through an overflow from which it is continuously distilled through a column filled with Raschig rings into a receiver 5.

10 The process according to the invention is illustrated by the following Examples.

EXAMPLE 1

15 100 g of crude titanium tetrachloride with a vanadium content of 680 ppm were introduced into a glass flask, and 1 g of aniline acting as the reducing agent was added. After brief shaking, the mixture was heated and the titanium tetrachloride immediately distilled off, without using a column except for a residue of about 20 %. After heating for about 3 to 5 minutes, and distillation for about 8 to 10 minutes, the distillate was tested for vanadium. The vanadium content was less than 1 ppm.

30

EXAMPLE 2

25 The suitability of a number of other amines for reducing VOCl_3 were tested as in Example 1. The quantities of vanadium found in the distillate are shown in the following Table which also shows the substances used. The starting material was once again a crude TiCl_4 containing 680 ppm of vanadium.

40	Compound added 1 g per 100 g of crude TiCl_4	Vanadium content of distillate (ppm)
	Piperidine	3
	2,3-dimethyl aniline	2
	Cyclohexylamine	4
45	N,N-dimethyl aniline	25
	2,6-dimethyl aniline	54

50 A rapid reaction occurred with these compounds, recognizable both from the formation of a discolored residue and from the reduced vanadium content of the distillate. By virtue of the fast reaction, the corresponding compounds are particularly suitable for removing vanadium from TiCl_4 .

55

EXAMPLE 3

60 A TiCl_4 of the kind which accumulates during the chlorination of rutile in the presence of carbon, having a solids content of 1.6% by weight and a vanadium content of 850 ppm, was introduced into a spherical flask equipped with a stirrer, column (30 cm) and dephlegmator, and 1% by weight of diphenyl amine was added. After heating to the boiling point, TiCl_4 was directly distilled off in colorless form. The vanadium content was analyzed and was less than 1 ppm. The distillate was colorless and did not show any signs of discoloration after a second distillation followed by 36 hours exposure to ultra violet light.

EXAMPLE 4

2 kg of a commercial-grade crude $TiCl_4$ obtained by chlorinating rutile, having a solids content of 1.6% by weight (1.1% by weight of carbon, 0.5% by weight of ash), an $FeCl_3$ content of 0.4% by weight, an $AlCl_3$ content of 0.1% by weight, an $MgCl_2$ content of 0.01% by weight and a vanadium content of 850 ppm, were introduced into a distillation flask, followed by the addition of 20 g of 2,6-dimethyl aniline. After heating to the boiling point over a period of about 10 minutes, a pale yellow-colored distillate containing less than 2 ppm of vanadium was directly obtained. After a further distillation, the distillate was colorless and could be used for the production of TiO_2 .

EXAMPLE 5

2 kg of commercial-grade crude $TiCl_4$ containing 680 ppm of vanadium were introduced into a spherical flask equipped with a dropping funnel, stirrer, column and dephlegmator, and 20 g of diphenylamine were added. Heating to the boiling point produced a reaction accompanied by the formation of a black deposit. The distillate was almost colorless and contained less than 1 ppm of vanadium. Crude $TiCl_4$ was introduced through the dropping funnel while distillation was still in progress. The distillate remained almost vanadium-free until about 0.6% by weight of diphenylamine had been consumed. Thereafter vanadium began to distil off. Accordingly, the diphenylamine requirement amounted to 1 mole for 3 moles of vanadium.

EXAMPLE 6

Crude $TiCl_4$ containing 680 ppm of vanadium was introduced into a spherical flask equipped with a stirrer, dropping funnel and dephlegmator, 1% by weight of aniline was added and the mixture was heated to its boiling point. More vanadium-containing crude $TiCl_4$ mixed with the corresponding quantity of aniline was added as distillation began. The impure commercial-grade $TiCl_4$ was added at a rate commensurate with that at which vanadium-free distillate was run off. In spite of the unfavorable residence time spectrum, it was possible to obtain vanadium-free $TiCl_4$ either pale blue or yellow in color. A crystal-clear titanium tetrachloride which contained less than 1 ppm of vanadium was obtained after a second distillation.

EXAMPLE 7

The commercial-grade crude $TiCl_4$ described in Example 4 was continuously purified using the apparatus as described hereinabove. The $TiCl_4$ formed was crystal clear, colorless and light-stable. Exposure to ultra violet light for more than 36 hours did not produce any discoloration.

The installation described above was operated continuously for 36 hours, producing 80 kg of pure $TiCl_4$ with a vanadium content of less than 1 ppm (detection limit of the analytical method used).

On the completion of the test, less than 0.02% of residue, based on the throughput, was isolated from the sump 3 of the distillation flask 4. In permanent operation, this residue would have had to be delivered to the flask 2 in the form of a recycle stream of the order of 1 to 2% of the $TiCl_4$ throughput. By varying the quantity of diphenylamine added to the $TiCl_4$, it was possible to detect 0.5 g diphenylamine per kg of $TiCl_4$ as the lower limit with 850 ppm of vanadium. If this lower limit was exceeded, the $TiCl_4$ in the flask 4 turned yellow in color

6 while the end product in the flask 5 turned yellow in color due to the $VOCl_3$. An excess of diphenylamine did not have any adverse effects.

EXAMPLE 8

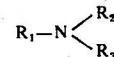
The installation described in Example 7 was operated for 14 hours using aniline as the reducing agent for $VOCl_3$. A crystal-clear colorless titanium tetrachloride of high light stability was formed with an addition of 1 g of aniline per kg of crude $TiCl_4$ (corresponding to Example 7). An excess of aniline was reflected by slight discoloration in the flasks 3 and 4, and a larger residue in the flask 4, and hence requires a larger recycle stream from 4 to 1 or 2.

15 If the addition of aniline is reduced to less than 0.6 g per kg of $TiCl_4$, vanadium breaks through, its presence being reflected in the yellowish color of the distillate in the flask 5.

20 It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. In the purification of impure vanadium-containing titanium tetrachloride comprising adding an agent to said titanium tetrachloride to react with the vanadium impurity and thereafter removing purified titanium tetrachloride as distillate while leaving the vanadium impurity-agent reaction product in the distillation residue, the improvement which comprises employing as said agent an amine of the formula



35 in which

R_1 and R_2 each independently is selected from the group consisting of hydrogen, alkyl of up to 6 carbon atoms, alkenyl of up to 6 carbon atoms, cycloalkyl of 5 to 7 carbon atoms, and aryl, and

40 R_3 is selected from the group consisting of cycloalkyl of 5 to 7 ring carbon atoms, and aryl.

45 2. In the purification of impure vanadium-containing titanium tetrachloride comprising adding an agent to said titanium tetrachloride to react with the vanadium impurity and thereafter removing purified titanium tetrachloride as distillate while leaving the vanadium impurity-agent reaction product in the distillation residue, the improvement which comprises employing as said agent at least one material selected from the group consisting of pyrrolidine and piperidine.

50 3. The process of claim 1, wherein R_3 is selected from the group consisting of cyclohexyl and phenyl.

55 4. The process of claim 3, wherein said agent is at least one material selected from the group consisting of cyclohexylamine, aniline, N,N-dimethyl-aniline, diphenylamine, 2,3-dimethyl-aniline and 2,6-dimethylaniline.

60 5. The process of claim 1, wherein said agent is added in about 0.1 to 10% by weight of the impure titanium tetrachloride.

65 6. The process of claim 1, wherein the impure titanium tetrachloride contains vanadium as an impurity and said agent is added within about 0.2 to 1.5% by weight of the impure titanium tetrachloride in about 0.1 to 5 times the molar amount of vanadium.

* * * * *